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Thesis

HEAVY METAL CHELATED COMPOUNDS OF BENZOYLNITROMETHANE AND SUBSTITUTED BENZOYLNITROMETHANES

by

Leon Eli Rubin

(B.S. Massachusetts Institute of Technology, 1942)

submitted in partial fulfilment of the

requirements for the degree of

Master of Arts

1947

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The author wishes to take this opportunity to express his appreciation for the generous aid and constructive criticism so kindly given by Dr. Richard H. Bailes throughout the course of this research.

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INTRODUCTION

The interest in heavy metal chelated compounds has been growing steadily throughout recent years. It was only in 1920, that Morgan (1) proposed the term "chelate" itself. From that time to the present more and more effort has been concentrated on these compounds. This Thesis is an attempt to open the study of the heavy metal chelated compounds of benzoylnitromethane and substituted benzoylnitromethanes.

The initial phase of this Thesis deals with the synthesis of benzoylnitromethane and some of its homologues. The reaction of aromatic aldehydes and nitromethane with potassium hydroxide as a condensing agent is well known. Thiele (2) used the reaction to prepare a number of nitrostyrenes in 1899. The procedure used was to treat the nitroalcohol formed by the condensation of the aldehyde and nitromethane with a mineral acid causing dehydration and the formation of the desired nitrostyrene. Other investigators (3-10) continued to expand the scope of the reaction. It was observed that the ease of condensation depends upon the nature and position, with respect to the aldehyde radical, of any substituting groups on the benzene ring. No generalization could be made from the results (4, 7), but the para hydroxyl group was found usually to prevent condensation. p-Aldehydophenoxyacetic acid, 3-nitro-4-hydroxybenzaldehyde and 5-nitro-3-aldehydosalicylic acid are examples of aldehydes that do not condense with nitromethane under the conditions of the reaction. Hahn and Stiehl (7) noted that not

only the position of the phenolic group but also the nature of the condensing agent plays a very material role in determining whether or not condensation will really take place. Vanillin was found to give only very little nitrostyrene with potassium hydroxide, but with methylamine it gave more than a 90% yield. Other aldehydes have shown this same tendency to condense under the influence of methylamine but not with potassium hydroxide. It is believed that salt formation which probably occurs with the alkali but not with the amine is the decisive factor. All nitrostyrenes without a phenolic group dissolve without color in 2N sodium hydroxide as the salt RCH(OH)CH NOONa, for immediate acidification precipitates the nitro alcohol $RCH(OH)CH_2NO_2$.

$$RCH{=}CHNO_2 + NaOH \rightarrow RCH(OH)CH{=}NOONa$$

Mineral acids or heat give a styrene $RCH\ CHNO_2$, more or less quantitatively, depending upon concentration, temperature, and the substituent on the benzene ring, but a part of the nitrostyrene is always broken down to aldehyde and nitromethane.

Holleman (11) was able to adapt the reaction for the isolation of the nitroalcohol by treating the sodium salt with acetic acid instead of a mineral acid. The nitroalcohol could then be oxidized to the ketone by the use of potassium dichromate in an acidic medium. This procedure was adopted for the preparation of the necessary ketones for this work.

The preparation of the nickel and copper complexes of the ketones followed the general procedure for preparing this class

of compounds. That is, merely by mixing a warm solution of a metal salt with that of the ketone and allowing the chelation complex to precipitate from the solution.

Chelate ring structures arise through the intramolecular coordination in systems involving a donor and acceptor center, or by intermolecular coordination in systems involving two or more coordinate linkages. The early work by Morgan and his collaborators (1, 13) showed the importance of ring closure and its bearing on chemical problems.

It should be recognized that the process of forming a chelate ring is essentially the same as forming a coordination link in an open chain compound. However the chelate ring systems of special interest in organic chemistry are those where cyclization introduces resonance effects or alters those already existant.

The evidence for the existence of chelated ring systems cannot be doubted. Experimental evidence derived from stereoisomerism, ionization phenomena, molecular association, solubility behavior, and spectroscopy all provide convincing proof of the formation of chelate ring complexes.

Sidgwick (14) has derived a method of classification of chelate rings into three types on the basis of the nature of the bonds that are present in the cyclic system. Type A includes those ring systems in which the coordinate link becomes identical with a normal covalent bond. Types B and C respectively contain one or two coordinate links. Diehl (15), on the other

hand, devised a system of classification based upon the number of atoms linked to the central metal atom. These main groups are then further broken down into subgroups depending on the number of covalent and coordinate linkages surrounding the central atom. As an example, type C, the tridentate group, is further sub-classified as 1C - three covalent linkages, 2C - two covalent linkages and one coordinate link, etc. The nickel and copper complexes of benzoylnitromethane and its homologues can be classified according to Sidgwick as type B, and according to Diehl as type D3.

In these classes the chelate structures most frequently encountered are five-membered rings containing one double bond and five- and six-membered rings containing two conjugated double bonds. Those with the six-membered rings are the most important found in organic chemistry. Due to favorable steric effects and the intervention of resonance effects, these rings are relatively stable. Either hydrogen or a metallic atom acts as the acceptor and usually oxygen or nitrogen acts as the donor atom. Typical examples of compounds in the same class as the benzoylnitromethanes are ortho substituted phenols, and the enolic forms of β-diketones and β-ketone esters. Many of the metallic derivatives of these substances are unusually stable. The beryllium, aluminum, and copper derivatives of acetylacetone can be distilled without appreciable decomposition.

It has long been the practice to try to coordinate the magnetic condition of the central nickel atom in complexes of

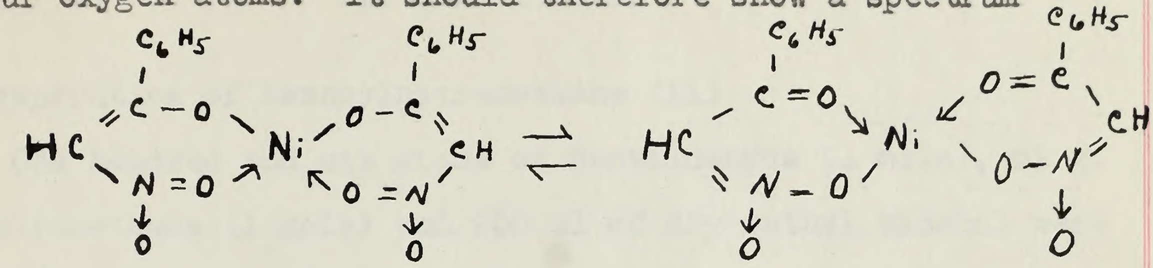
this type with the color of the compound itself. As a rule it had been assumed in the past that paramagnetic nickel complexes would be green or blue, while diamagnetic complexes would be reddish-brown or yellow. But little faith can now be held in this generalization (16) since many green diamagnetic compounds have been prepared in this laboratory.

It has been postulated by Mellor and his collaborators (17, 18) that the spectra of diamagnetic nickel complexes exhibits the following features when compared with the spectra (light absorption) of the organic addenda or chelate groups: (1) the bands of the chelated complex are slightly displaced, usually towards higher wave lengths, and (2) a band of appreciable intensity is observed which must be attributed to the nickel atom. On the other hand, the paramagnetic complexes of nickel show no band which can be attributed to nickel, and the absorption bands of the complexes appear to be those of the organic molecule displaced and considerably broadened.

It may be noted that the spectrum of the sodium salt of the organic addendum bears a great resemblence to that of a paramagnetic complex of nickel itself. Also complexes belonging to the class that has nickel linked to four oxygen atoms are always paramagnetic; if linked to four nitrogen or four sulfur atoms always diamagnetic, while if linked to two nitrogen and two oxygen atoms either paramagnetic or diamagnetic.

The nickel complexes of benzoylnitromethane and its homologues belong to the class that has the nickel atom linked

to four oxygen atoms. It should therefore show a spectrum



indicative of paramagnetic complexes of nickel. That is, of course, the nickel atom itself should make very little contribution to the spectrum of the nickel complex.

This Thesis includes the study of the spectra of benzoylnitromethane, p-methoxybenzoylnitromethane, p-nitrobenzoylnitromethane, m-nitrobenzoylnitromethane, m-tolylnitromethane, o-chlorobenzoylnitromethane and their nickel complexes. The observed spectra will give important clues as to the magnetic condition of the nickel atom, and the effect of the nature and the position of the substituent groups on the benzene ring may be evaluated.

The work of this Thesis, therefore, was to prepare the nickel complexes of benzoylnitromethane and the substituted benzoylnitromethanes, study their solubilities, solvation by various solvents, and their absorption spectra in the visible and ultraviolet regions and compare the spectra with each other and with the spectra of the organic addenda of the nickel complexes.

II. EXPERIMENTAL

1. Preparation of Benzoylnitromethane (11)

One hundred and six grams of benzaldehyde (1 mole), 61 g. of nitromethane (1 mole) and 200 ml of dry methyl alcohol were cooled in an ice-salt bath to 13°C. Seventy grams of potassium hydroxide in 265 ml of methyl alcohol was cooled and added dropwise to the mixture. During the addition, the solution became yellow, and the temperature rose to 29°C. The solution was cooled to 17°C and kept below a temperature of 20°C for the remainder of the addition of the potassium hydroxide. A large quantity of white crystals settled out, and the stirring was continued for one-half hour. The sodium phenyl nitromethyl carbinol (58 g.) was filtered, washed with a small quantity of methyl alcohol, dissolved in ice-water and acidified with 20 ml of 25% acetic acid. The yellow oil, which appeared at this point, was separated. The water solution was extracted with three 30 ml portions of ether, which were combined with the oil. The combined ether-oil solution was washed successively with 50 ml of water, 50 ml of 10% sodium bicarbonate solution, and 50 ml of water and dried for 24 hours over 25 g. of anhydrous sodium sulfate. The ether-phenyl nitromethyl carbinol solution was decanted, and the ether removed by evaporation at room temperature in vacuo. Yield of the light red-brown (crude) phenyl nitromethyl carbinol was 56 g. (33.4%).

$$C_6H_5CHO + H_3CNO_2 \xrightarrow{KOH} C_6H_5CH(OH)CH{=}NOOK$$

$$C_6H_5CH(OH)CH=NOOK + H_3CCOOH \rightarrow C_6H_5CH(OH)CH_2NO_2$$

Phenyl nitromethyl carbinol (3.4 g.) was oxidized by a mixture of 4 g. of potassium dichromate in 20 ml of water and 2 ml of concentrated sulfuric acid. The carbinol was cooled in an ice bath and the dichromate solution was added at such a rate that the temperature remained below 25° C. After 20 minutes the solution, which had become dark, was removed from the cooling bath and let stand at room temperature for 24 hours.

The crude benzoylnitromethane was filtered, washed with water, dissolved in warm alcohol, treated with "Norite", and precipitated by the addition of water. The ketone was recrystallized twice more from alcohol. Yield was 1.2 g. (34.0%) of white plates melting at 105-106° C.

2. Preparation of m-Toluylnitromethane

Forty grams of m-tolualdehyde (0.33 mole) and 21 g. of nitromethane (0.33 mole), cooled to 0° C, were condensed under the influence of 23 g. of potassium hydroxide in 70 ml of dry methyl alcohol. The procedure followed was essentially the same as in section 1, with the exception that the greater quantity of the methyl alcohol present was removed by evaporation in vacuo before the sodium salt of the m-tolyl nitromethyl carbinol was filtered. A yield of 49.7 g. (83.3% crude) of light yellow carbinol was obtained.

The m-tolyl nitromethyl carbinol distills as a crystal-clear liquid at 52-53° C at a pressure of less than 1 mm Hg. Upon standing in air the carbinol becomes red-yellow in color.

Attempted oxidation of 4 g. of the crude carbinol by 4 g. of potassium dichromate in 20 ml of water and 2 ml of concentrated sulfuric acid under the same conditions as noted in section 1 was unsuccessful.

Further investigation along the lines of dichromate oxidation showed that a reaction period of 6 days results in an approximate yield of 2 to 3% of straw colored crystals of m-toluylnitromethane.

Ten grams of crude carbinol in 30 ml of glacial acetic acid was oxidized by 3.1 g. of chromium trioxide in 150 ml of glacial acetic acid and 10 ml of water. The chromium trioxide solution was added dropwise and was accompanied by a rise in temperature from 25° to 32° C. The solution was allowed to stand for 72

hours during which time it became dark green in color. The solution was diluted with 500 ml of water and a yellow precipitate appeared. This precipitate was filtered, washed with water, and recrystallized from alcohol. A yield of 0.3 g. (3 %) of colorless crystals of m-toluylnitromethane was obtained.

3. Preparation of p-Nitrobenzoylnitromethane (25)

p-Nitrophenyl nitromethyl carbinol was prepared in 82.2% yield (crude) by condensing 18.5 g. of p-nitrobenzaldehyde (0.11 mole) with 7 g. of nitromethane (0.11 mole) in 45 ml of methyl alcohol under the action of 8 g. of potassium hydroxide in 32 ml of methyl alcohol. The procedure is the same as found in section 1. The carbinol is a light yellow solid melting at 78-79° C.

Oxidation of 4 g. of p-nitrophenyl nitromethyl carbinol by 4 g. of potassium dichromate in 20 ml of water and 2 ml of concentrated sulfuric acid for a period of 5 days at room temperature resulted in a 25% yield of straw-yellow p-nitrobenzoylnitromethane, mp. 227-228.5° C.

4. Preparation of o-Chlorobenzoylnitromethane

Fifty-seven grams of o-chlorobenzaldehyde (0.4 mole) and 24.4 g. of nitromethane (0.4 mole) condensed by the usual method with 28 g. of potassium hydroxide in 70 ml of methyl alcohol gave crude o-chlorophenyl nitromethyl carbinol in 93.6% yield (55.4 g.)

Oxidation of 4 g. of this carbinol by 4 g. of potassium dichromate in 20 ml of water and 2 ml of concentrated sulfuric acid for 4 days at room temperature gave white leaflets of o-chlorobenzoylnitromethane, mp. 129-132° C, in an 18% yield.

Oxidation of 8 g. of the carbinol in 40 ml of glacial acetic acid with 3.2 g. of chromium trioxide in 115 ml of glacial acetic acid and 10 ml of water for 48 hours at room temperature resulted in a 5% yield of whitish o-chlorobenzoylnitromethane mp. 130-132° C.

5. Preparation of p-Methoxybenzoylnitromethane (8)

p-Methoxyphenyl nitromethyl carbinol* is a heavy yellow liquid boiling at 110-111° C at 4 mm Hg with an index of refraction n_D^{20} equal to 1.5596.

Four grams of p-methoxyphenyl nitromethyl carbinol was oxidized by 4 g. of potassium dichromate in 20 ml of water and 2 ml of concentrated sulfuric acid in the usual manner for 24 hours at room temperature. After purification 0.6 g. (15%) yield of yellow plates mp. 154-155.5° C was obtained.

---

* The crude p-methoxyphenyl nitromethyl carbinol was prepared in this laboratory by Miss Helen Elliot.

6. Preparation of m-Nitrobenzoylnitromethane

m-Nitrophenyl nitromethyl carbinol* is a yellow solid, mp. 52-54° C, distilling at 122-124° C at mm Hg as a green-yellow liquid.

Oxidation of 3.5 g. of m-nitrophenyl nitromethyl carbinol by 4 g. of potassium dichromate in 20 ml of water and 2 ml of concentrated sulfuric acid in the usual manner for 4 days gave, after purification, a 0.5 g. (14.1%) yield of white feathery crystals mp. 114-115° C.

Attempted oxidation of 5 g. of crude carbinol by 3 g. of potassium permanganate in 40 ml of water and 20 ml of 10% sodium hydroxide for 24 hours at room temperature was unsuccessful.

Attempted oxidation of 5 g. of crude carbinol by 3 g. of potassium permanganate in 40 ml of water for 24 hours at room temperature was unsuccessful.

Attempted oxidation of 5 g. crude carbinol by 6.8 g. of 3% hydrogen peroxide in 10 ml of water and 20 ml of 10% sodium hydroxide for 2 hours at room temperature yielded only a very small amount of product. The amount of product obtained was insufficient to warrant purification.

Five grams of crude carbinol in 30 ml of glacial acetic

* The crude m-nitrophenyl nitromethyl carbinol was prepared in this laboratory by Miss Helen Elliot.

acid was oxidized by 1.6 g. of chromium trioxide in 160 ml of glacial acetic acid and 20 ml of water. A rise in temperature from 24° to 30° C was observed during the dropwise addition of the chromium trioxide solution. To complete the reaction, the solution was allowed to stand at room temperature for 24 hours. The solution was diluted with 500 ml of cold water and extracted successively with 100, 50, and 50 ml of benzene. The yellow benzene solution was dried over anhydrous potassium carbonate and evaporated to a tarry mass. This mass was taken up in alcohol and a white solid was precipitated by the addition of water. Fine white needles mp. 114-115° C were obtained in a yield of 0.2 g. (5.7%).

7. Solubility Characteristics of the Substituted Benzoylnitromethanes and Solid Carbinols

The tests for the solubilities of the compounds named below were carried out in a purely qualitative manner. Small amounts of the compounds were immersed in the various solvents, both hot and cold. Visually it was noted whether or not the solution became colored or if the amount of solid compound decreased.

TABLE I

	Solubility	
SOLVENT	a Benzoylnitromethane	b o-Chlorobenzoylnimethane
Cold water	insol.	insol.
Hot water	sl. sol.	insol.
Cold ether	sol.	insol.
Warm ether	sol.	sl. sol.
Cold acetic acid	sol.	sl. sol.
Hot acetic acid	sol.	sol.
Cold alcohol	sol.	sol.
Hot alcohol	sol.	sol.
Cold benzene	sol.	sol.
Hot benzene	sol.	sol.

TABLE I (Continued)

SOLVENT	c p-Methoxybenzoylnitromethane	d p-Nitrobenzoylnitromethane
Cold water	insol.	insol.
Hot water	sl. sol.	insol.

TABLE I (Continued)

SOLVENT	c p-Methoxybenzoyl-nitromethane	d p-Nitrobenzoyl-nitromethane
Cold ether	sl. sol.	sol.
Warm ether	sol.	sol.
Cold acetic acid	sol.	sl. sol.
Hot acetic acid	sol.	sol.
Cold alcohol	sl. sol.	sl. sol.
Hot alcohol	sol.	sol.
Cold benzene	sol.	sl. sol.
Hot benzene	sol.	sl. sol.

TABLE I (Continued)

SOLVENT	e m-Nitrobenzoyl-nitromethane	f m-Toluylnitro-methane
Cold Water	insol.	insol.
Hot water	insol.	sl. sol.
Cold ether	insol.	insol.
Hot ether	sl. sol.	sl. sol.
Cold acetic acid	insol.	insol.
Hot acetic acid	insol.	insol.
Cold alcohol	sol.	sol.
Hot alcohol	sol.	sol.
Cold benzene	sol.	sol.
Hot benzene	sol.	sol.

TABLE I (Continued)

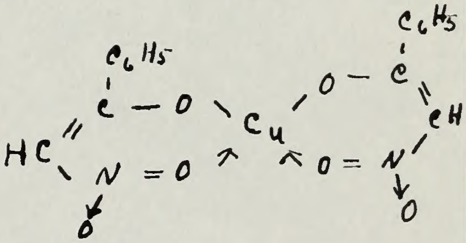
SOLVENT	g p-Nitrophenyl Nitromethyl Carbinol	h m-Nitrophenyl Nitromethyl Carbinol
Cold water	insol.	insol.
Hot water	sl. sol.	sol.
Cold ether	insol.	sol.
Hot ether	insol.	sol.
Cold acetic acid	sol.	sol.
Hot acetic acid	sol.	sol.
Cold alcohol	sol.	sol.
Hot alcohol	sol.	sol.
Cold benzene	insol.	sl. sol.
Hot benzene	sol.	sol.

8. Copper Benzoylnitromethane

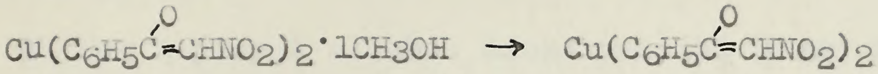
A solution of 1.2 g. of copper acetate (0.006 mole) in 30 ml of water (45° C) was added to 1 g. benzoylnitromethane (0.006 mole) in 30 ml of methyl alcohol (44° C). A green flocculent precipitate appeared after five minutes. The precipitate was filtered, washed in cold water (crystals slowly becoming brown), recrystallized from pyridine, washed with cold water, and dried in vacuo over calcium chloride. A 75% (1.8 g.) yield of brown copper benzoylnitromethane, decomposing at 187° C, was obtained.

	Analysis		
was obtained.	Analysis Calculated	Cu	16.33%
	Found	Cu	16.2%

$2C_6H_5COCH_2NO_2$ + $(CH_3COO)_2CU$ →



It should be noted that on preparing this copper salt in a 50-50 methyl alcohol and water solution, green crystals result. A sample of these green crystals was dried in vacuo over calcium chloride until its weight became constant. Green copper benzoylnitromethane (0.2675 g.) was heated in vacuo at 80° C for 1 hour. The resulting crystals were red-brown in color and weighed 0.2473 g. The loss in weight corresponds to 1 CH_3OH (0.0202 g. or 7.55% by weight); theoretical loss in weight for 1 CH_3OH being 7.46%.



$$Cu(C_6H_5\overset{O}{C}=CHNO_2)_2\cdot 1CH_3OH \rightarrow Cu(C_6H_5\overset{O}{C}=CHNO_2)_2$$

Green   Brown

A sample of the brown or unsolvated form of copper benzoylnitromethane was heated in n-butyl alcohol, and all excess undissolved copper salt was filtered off. Upon cooling the solution with a water-ice bath, green crystals appeared. The crystals were filtered and placed to dry in a desiccator over calcium chloride. Overnight the crystals lost their solvated butyl alcohol and became brown. It was then found that standing in air for 30 minutes is sufficient for the salt solvated with n-butyl alcohol to start losing its green color. A sample of the green form of copper benzoylnitromethane (0.9709 g.), air-dried for 15 minutes, was heated in vacuo at 135° C for 45 minutes. A loss in weight of 19.5% (0.1902 g.) and a color change from green to brown was found. Theoretical loss of weight calculated for loss of one molecule of butanol is 17.0%. The discrepancy is due to the fact that the solvated form loses its one molecule of butanol so rapidly that it could not be dried thoroughly.

The results of tests determining the reaction of the brown and green forms of copper benxoylnitromethane are summarized here below.

a. Methanol and the brown crystals give a green form (slow in the cold; rapidly when heated)

b. Absolute ethyl alcohol (when heated) and the brown form

give the green.

c. Hot n-propyl alcohol dissolves the brown form; on cooling the brown crystals reappear.

d. Isopropyl alcohol has no effect on the brown form.

e. n-Butyl alcohol, when warm, dissolves the brown form, and on cooling, a green form precipitates.

f. Isobutyl alcohol, when warm, dissolves the brown form to give a green form on cooling.

g. Sec.-butyl alcohol will dissolve the brown form.

h. Tert.-butyl alcohol has no effect on the brown form.

i. The brown form is soluble in cold acetone.

The green crystals indicated in the tests below were prepared by the solvation of the brown form with methyl alcohol.

a. Warm chloroform changes the green form to the brown.

b. Benzene, ether, and n-propyl alcohol in the cold rapidly convert the green form to the brown.

c. The green form, when heated with ligroin, turn brown.

d. Toluene, isopropyl alcohol, carbon tetrachloride and xylene will change the green form to the brown.

e. The green crystals are soluble in isobutyl alcohol.

f. Acetone dissolves the green form to give a green solution. The brown form crystallizes from the acetone solution.

Copper benzoylnitromethane on standing in cold dilute sulfuric acid slowly decomposes to give a white solid mp. 121° C (benzoic acid mp. 122° C). Dilute acetic acid and the copper salt give a green solution (copper ions). Ten per cent sodium

hydroxide also causes decomposition leaving a light blue solution, while dilute ammonium hydroxide causes the formation of the dark blue cupric ammonia complex ion.

9. Copper Chelated Compounds of the Substituted Benzoylnitromethanes

Yellow-brown copper p-methoxybenzoylnitromethane (analysis calcd. - Cu 14.2%. found - Cu 14.3%) in 60% yield, dark green copper m-nitrobenzoylnitromethane (analysis calcd. - Cu 13.2%, found - Cu 13.3%) in 72% yield, green copper m-toluylnitromethane (analysis calcd. - Cu 15.2%, found - Cu 15.4%) in 51% yield, green copper p-nitrobenzoylnitromethane (analysis calcd. - Cu 13.3%, found - Cu 13.2%) in 55% yield, and light green copper o-chlorobenzoylnitromethane (analysis calcd. - Cu 13.6%, found - Cu 13.2%) in 78% yield were prepared in the same manner as previously described for copper benzoylnitromethane.

Each of the compounds named above was crystallized from methyl alcohol, ethyl alcohol, and pyridine. After recrystallization and drying in vacuo over calcium chloride to a constant weight, a weighed sample of each compound was heated in vacuo at 80° C or 100° C or 161° C for 1 hour, depending on what solvent was used for recrystallization. In every case no solvation of the chelated compound by methanol, ethanol, or pyridine could be detected either by loss of weight or by a change of color. Melting point determinations showed that none of these compounds melt or decompose below 200° C.

The following table shows the solubility characteristics of these compounds. As in Table I (page 16), these results are only a qualitative measure. The procedure was the same as that described earlier for Table I.

TABLE II

Solubility Characteristics of the Copper Chelated Compounds of Substituted Benzoylnitromethanes

SOLVENT	a Copper p-Methoxybenzoylnitromethane	b Copper m-Nitrobenzoylnitromethane
Cold methanol	--	insol.
Hot methanol	--	sol.
Cold ethanol	sl. sol.	sl. sol.
Hot ethanol	sol.	sol.
Cold n-propyl alcohol	insol.	--
Hot n-propyl alcohol	sl. sol.	--
Cold butyl alcohol	insol.	insol.
Hot butyl alcohol	sl. sol.	sl. sol.
Cold amyl alcohol	insol.	--
Hot amyl alcohol	sl. sol.	--
Cold acetone	sl. sol.	sol.
Hot acetone	sol.	sol.
Cold carbon tetrachloride	insol.	insol.
Hot carbon tetrachloride	sl. sol.	insol.
Cold toluene	insol.	insol.
Hot toluene	sl. sol.	insol.
Cold benzene	--	insol.
Hot benzene	--	insol.
Cold pyridine	sol.	sol.
Hot pyridine	sol.	sol.
Cold chloroform	--	sol.
Hot chloroform	--	sol.

TABLE II (Continued)

SOLVENT	c Copper m-Toluylnitromethane
Cold methanol	sl. sol.
Hot methanol	sol.
Cold ethanol	sl. sol.
Hot ethanol	sl. sol.
Cold butyl alcohol	insol.
Hot butyl alcohol	sol.
Cold acetone	sol.
Hot acetone	sol.
Cold carbon tetrachloride	--
Hot carbon tetrachloride	--
Cold toluene	sol.
Hot toluene	sol.
Cold benzene	sl. sol.
Hot benzene	sol.
Cold pyridine	sol.
Hot pyridine	sol.
Cold chloroform	sol.
Hot chloroform	sol.

TABLE II (Continued)

SOLVENT	d Copper p-Nitrobenzoylnitromethane	e Copper o-Chlorobenzoylnitromethane
Cold methanol	sol.	sl. sol.
Hot methanol	sol.	sl. sol.
Cold ethanol	sol.	sol.
Hot ethanol	sol.	sol.
Cold butyl alcohol	sol.	insol.
Hot butyl alcohol	sol.	sol.
Cold acetone	sol.	sol.
Hot acetone	sol.	sol.
Cold carbon tetrachloride	insol.	insol.
Hot carbon tetrachloride	insol.	insol.
Cold toluene	insol.	insol.
Hot toluene	insol.	insol.
Cold benzene	insol.	insol.
Hot benzene	insol.	insol.
Cold pyridine	sol.	sol.
Hot pyridine	sol.	sol.
Cold chloroform	insol.	sol.
Hot chloroform	insol.	sol.
Cold ether	insol.	--
Hot ether	insol.	--

It was found that the copper chelated compounds of the substituted benzoylnitromethanes on standing for 24 hours in

cold dilute mineral acid decompose and deposit benzoic acid. Cold dilute acetic acid, dilute ammonium hydroxide and 10% sodium hydroxide readily decompose the complexes. The acetic acid solution turns green; the sodium hydroxide solution, light blue; and ammonium hydroxide, the dark blue of the cupric ammonia complex ion.

10. Nickel Chelated Compounds of Benzoylnitromethane and Substituted Benzoylnitromethanes

Green nickel benzoylnitromethane (analysis calcd. - Ni 15.03%, found - Ni 15.15%) in 53% yield, red-brown nickel m-nitrobenzoylnitromethane (analysis calcd. - Ni 11.4%, found - Ni 11.25%) in 68% yield, yellow-green nickel p-nitrobenzoylnitromethane (analysis calcd. - Ni 11.4%, found - Ni 11.1%) in 81% yield, green nickel m-toluylnitromethane (analysis calcd. - Ni 14.2%, found - Ni 14.4%) in 74% yield, yellow-green nickel p-methoxybenzoylnitromethane (analysis calcd. - Ni 13.3%, found - Ni 13.2%) in 48% yield and yellow-brown nickel o-chlorobenzoylnitromethane (analysis calcd. - Ni 12.7%, found - Ni 12.4%) in 55% yield were prepared in an analogous manner as in the preparation of the copper chelated compounds.

Each of the nickel compounds prepared above was heated in methanol and dried in vacuo to a constant weight. A weighed sample of each of the so-treated compounds was heated in vacuo at 80° C or 161° C, depending on which solvent with which the compound was treated. No evidence of solvation of any of the nickel complexes by methanol or pyridine could be detected either by loss in weight or by a change of color. Melting point determinations showed that none of these compounds melt or decompose below 200° C.

Hot dilute mineral acids decompose the nickel chelates. A dark oil appears, and the acid layer, when neutralized with ammonium hydroxide, shows the presence of nickel by the

dimethylglyoxime precipitate. Acetic acid when hot also decomposes these complexes and a deposit of a white solid is obtained. This solid has the same melting point as benzoic acid, and a mixed melting point of solid-benzoic acid shows no depression. The chelates are stable towards 10% sodium hydroxide in the cold, but rapidly decompose when heated to boiling. Cold dilute ammonium hydroxide slowly decomposes the nickel complexes.

The following table briefly outlines the solubility characteristics of these nickel complexes. The procedure used to obtain these values are the same as was described for Table I (page 16).

TABLE III

Solubility Characteristics of Nickel Chelated Compounds of Benzoylnitromethane and Substituted Benzoylnitromethanes

SOLVENT	a Nickel Benzoylnitromethane	b Nickel p-Methoxybenzoylnitromethane
Cold methanol	sl. sol.	sl. sol.
Hot methanol	sl. sol.	sl. sol.
Cold ethanol	sl. sol.	v. sl. sol.
Hot ethanol	sl. sol.	sl. sol.
Cold propanol	--	insol.
Hot propanol	--	sl. sol.
Cold butanol	--	insol.
Hot butanol	--	sol.
Cold amyl alcohol	--	insol.
Hot amyl alcohol	--	sol.

TABLE III (Continued)

SOLVENT	a Nickel Benzoyl-nitromethane	b Nickel p-Methoxybenzoylnitromethane
Cold acetone	sol.	sl. sol.
Hot acetone	sol.	sol.
Cold chloroform	sol.	insol.
Hot chloroform	sol.	sol.
Cold carbon tetrachloride	insol.	insol.
Hot carbon tetrachloride	sl. sol.	sl. sol.
Cold toluene	insol.	insol.
Hot toluene	sol.	sl. sol.
Cold benzene	sl. sol.	--
Hot benzene	sol.	--
Cold pyridine	sol.	sol.
Hot pyridine	sol.	sol.

TABLE III (Continued)

SOLVENT	c Nickel m-Nitrobenzoylnitromethane	d Nickel m-Toluyl-nitromethane
Cold methanol	sl. sol.	sl. sol.
Hot methanol	sol.	sol.
Cold ethanol	sl. sol.	sl. sol.
Hot ethanol	sol.	sol.
Cold butanol	sl. sol.	sol.
Hot butanol	sol.	sol.
Cold acetone	sl. sol.	sol.
Hot acetone	sol.	sol.

TABLE III (Continued)

SOLVENT	c Nickel m-Nitrobenzoylnitromethane	d Nickel m-Toluylnitromethane
Cold chloroform	sl. sol.	sol.
Hot chloroform	sol.	sol.
Cold carbon tetrachloride	sl. sol.	sl. sol.
Hot carbon tetrachloride	sol.	sl. sol.
Cold toluene	insol.	sol.
Hot toluene	sol.	sol.
Cold benzene	insol.	sol.
Hot benzene	v. sl. sol.	sol.
Cold pyridine	sol.	sol.
Hot pyridine	sol.	sol.

TABLE III (Continued)

SOLVENT	e Nickel p-nitrobenzoylnitromethane	f Nickel o-Chlorobenzoylnitromethane
Cold methanol	sol.	sol.
Hot methanol	sol.	sol.
Cold ethanol	sl. sol.	sol.
Hot ethanol	sl. sol.	sol.
Cold butanol	insol.	sl. sol.
Hot butanol	sl. sol.	sol.
Cold acetone	sol.	sol.
Hot acetone	sol.	sol.
Cold chloroform	insol.	sol.

TABLE III (Continued)

SOLVENT	e Nickel p-Nitrobenzoylnitromethane	f Nickel o-Chlorobenzoylnitromethane
Hot chloroform	insol.	sol.
Cold toluene	insol.	sl. sol.
Hot toluene	insol.	sol.
Cold benzene	insol.	sol.
Hot benzene	sl. sol.	sol.
Cold pyridine	sol.	sol.
Hot pyridine	sol.	sol.
Cold carbon tetrachloride	insol.	insol.
Hot carbon tetrachloride	insol.	insol.
Cold ether	insol.	sol.
Hot ether	sl. sol.	sol.

11. Absorption Spectra

The absorption spectra, in the visible and the ultraviolet ranges, of the nickel chelated complexes and the parent ketones, from which the complexes were derived, were determined with the Beckman model DU photoelectric quartz spectrophotometer. A hydrogen discharge lamp (#2230 coupled with a hydrogen lamp power supply #2220) served as the light source for the range 220 to 320 millimicrons, and a tungsten lamp was used from 320 to 1000 millimicrons.

A calculated quantity of each of the nickel chelated complexes and ketones prepared in this thesis was dissolved in an exact amount of absolute alcohol (volumetric flasks were used) to give the solution concentrations as noted on the accompanying graphs and tables. Solutions in the concentration range 10^{-3} to 10^{-6} were necessary due to the fact that neither more concentrated nor more dilute solutions would give satisfactory results on the spectrophotometer using a 10 mm light path.

The absolute alcohol was prepared by drying commercial absolute alcohol over Drierite for 48 hours and distilling through a 22 inch fractionating column.

The Beckman spectrophotometer measures the per cent transmission of light of any one wavelength of any solution balanced against a blank containing only the solvent. This transmission (T) is a measure of the light intensity transmitted

(I) by the material as compared to the intensity of the incident beam (I_0) corrected for the presence of solvent, in this case absolute alcohol, $T=I/I_0$. The opacity of the solution is then the ratio I_0/I and the term density (measured directly by the spectrophotometer) is the $-\log_{10} I/I_0$. The extinction coefficient as defined by Bunsen and Rosco (26) is

$$ecd = -\log_{10} I/I_0 = D$$

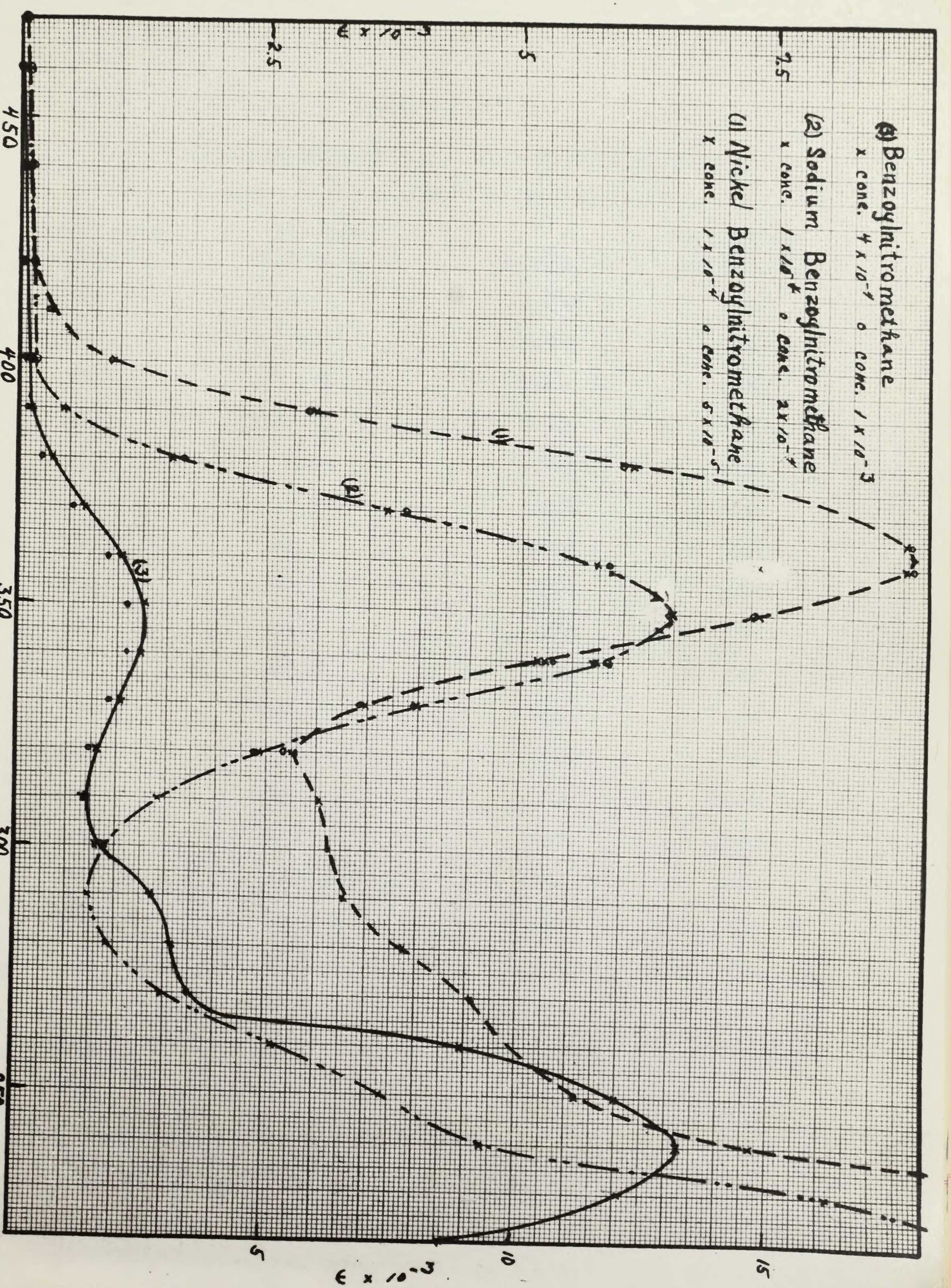
where c is the concentration in moles per liter; d, the length of the light path in centimeters; D, the density; and e, the molar extinction coefficient.

Since the light path in all cases was 1.00 cm, the extinction coefficient was calculated by dividing the density by the concentration of the solution.

The absorption spectra curves and data for all the ketones and nickel complexes as well as the sodium salts of benzoylnitromethane and p-methoxybenzoylnitromethane and nickel acetate will be found in Fig. 1 - 6 and Tables IV - XVIII following.

The sodium salts above were prepared by adding a 20-fold excess of sodium ethoxide to solutions of the ketones. The nickel acetate solution was prepared by dissolving 0.0498 g. $Ni(CH_3COO)_2 \cdot 4H_2O$ in 75 ml of absolute alcohol and the volume of the solution was brought to 100 ml.

Fig. 1



Curve 3 use ordinate at left

TABLE IV

Absorption Spectra for Benzoylnitromethane

Concentration 4 x 10^{-4} moles per liter

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
220	1.92	1.713	4280
230	.35	2.42	6050
240	.21	2.65	6625
250	.38	2.40	6000
260	1.62	1.788	4470
270	20.0	.698	1745
280	23.0	.638	1595
290	28.3	.548	1370
300	48.5	.319	798
310	54.5	.263	660
320	47.6	.322	805
330	38.6	.414	1035
340	32.1	.494	1235
350	31.3	.504	1260
360	38.5	.414	1040
370	54.5	.263	660
380	77.8	.107	268
390	92.7	.033	82
400	97.8	.009	22
410	99.2	.0035	8

TABLE IV (Continued)

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
420	99.5	.0025	6
440	99.5	.0025	6
460	100	.000	0
	Concentration 1 x 10^{-3} Moles per Liter		
320	18.5	.732	730
330	12.1	.915	915
340	8.5	1.070	1070
350	8.42	1.074	1074
360	13.2	.888	888
370	28.8	.540	540
380	61.7	.210	210
390	87.7	.060	60
400	96.2	.017	17
410	98.8	.006	6
420	99.5	.0025	2.5
440	99.7	.002	2
460	100	.000	0

TABLE V

Absorption Spectra of Sodium Benzoylnitromethane

Concentration 1 x 10^{-4} Moles per Liter

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
220	.70	2.16	21600
230	2.4	1.620	16200
240	11.5	.935	9350
250	18.4	.735	7350
260	30.3	.518	5180
270	50.8	.293	2930
280	65.2	.186	1860
290	71.3	.147	1470
300	66.8	.175	1750
310	52.3	.282	2820
320	32.8	.484	4840
330	15.8	.798	7980
340	7.23	1.142	11420
350	5.2	1.298	12980
360	7.3	1.137	11370
370	18.6	.732	7320
380	49.5	.304	3040
390	83.0	.082	820
400	94.5	.025	250
420	97.9	.008	80
440	98.1	.007	70

TABLE V (Continued)

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
500	98.2	.0065	65
600	98.8	.005	50
700	98.8	.005	50
900	98.9	.004	40
	Concentration 2 x 10^{-4} Moles per Liter		
320	11.3	.945	4725
330	2.6	1.585	7925
340	.48	2.32	11600
350	.25	2.58	12900
360	.46	2.34	11700
370	2.78	1.555	7770
380	21.3	.668	3340
390	67.0	.174	870
400	90.2	.045	225
420	97.9	.008	40
440	98.5	.006	30
500	99.0	.004	20
600	99.6	.002	10
700	99.5	.002	10
900	99.7	.001	5

TABLE VI

Absorption Spectra of Nickel Benzoylnitromethane

Concentration 1×10^{-4} Moles per Liter

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
230	.45	2.35	23500
240	3.38	1.469	14690
250	7.70	1.12	11200
260	7.10	1.15	11500
270	11.8	.913	9130
280	16.8	.775	7750
290	22.2	.652	6520
300	23.5	.628	6280
320	28.4	.546	5460
330	20.2	.695	6950
340	9.4	1.03	10300
350	3.42	1.466	14660
360	1.75	1.755	17550
365	1.76	1.753	17530
380	6.13	1.213	12130
390	25.8	.592	5920
400	64.75	.189	1890
410	86.3	.063	630
420	94.2	.027	270
440	98.5	.007	70
450	99.2	.0035	35

TABLE VI (Continued)

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
460	99.5	.0025	25
470	99.5	.0025	25
490	99.7	.002	20
510	100	.000	0
	Concentration 5 x 10^{-5} Moles per Liter		
320	54.2	.266	5320
330	45.3	.343	6860
340	26.6	.574	11480
350	18.7	.727	14540
360	13.5	.885	17700
365	13.75	.882	17640
380	25.2	.597	11940
390	51.8	.285	5700
400	81.1	.093	1860
410	93.3	.029	580
420	97.2	.013	260
440	99.2	.0035	70
450	99.7	.002	40
460	100	.000	0

Fig. 2

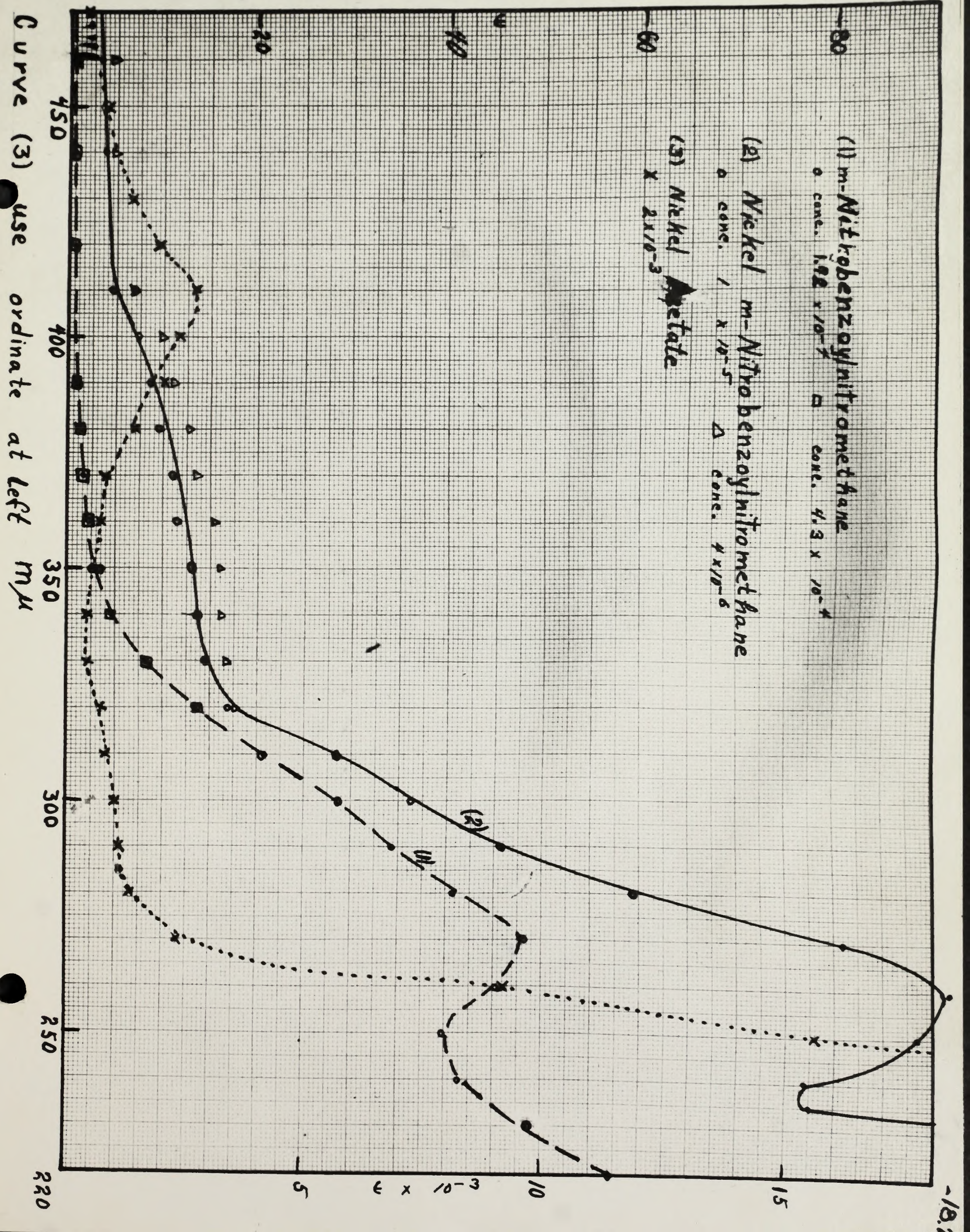

(1) m-Nitrobenzoylnitromethane
○ conc. 1.98 × 10^-4 □ conc. 4.3 × 10^-4
(2) Nickel m-Nitrobenzoylnitromethane
○ conc. 1 × 10^-5 △ conc. 4 × 10^-6
(3) Nickel Acetate
× 2×10^-3
(1)
(2)
ε
20
40
60
80
450
400
350
300
250
220
5
ε × 10^-3
10
15
-18.
Curve (3) use ordinate at left
mμ

TABLE VII

Absorption Spectra of m-Nitrobenzoylnitromethane

Concentration 1.72 x 10^{-4} Moles per Liter

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
220	1.12	1.95	11450
230	2.08	1.678	9755
240	3.77	1.423	8273
250	4.31	1.364	7930
260	2.81	1.55	9010
270	2.2	1.657	9635
280	4.01	1.397	8122
290	6.58	1.182	6872
300	10.6	.988	5744
310	19.4	.710	4130
320	33.6	.474	2755
330	51.3	.290	1686
340	69.6	.157	910
350	79.2	.102	580
360	84.5	.073	424
370	88.6	.052	302
380	91.7	.037	215
390	94.0	.027	155
400	95.7	.018	103
420	97.3	.012	67
440	98.2	.007	41

TABLE VII (Continued)

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
460	98.5	.006	35
500	99.2	.004	23
550	99.3	.003	17
600	99.5	.002	12
700	100	.000	0
Concentration 4.3×10^{-4} Moles per Liter			
320	6.47	1.190	2770
330	19.0	.720	1674
340	40.5	.3925	910
350	55.5	.255	600
360	65.5	.184	428
370	73.7	.132	307
380	80.3	.093	216
390	86.0	.066	154
400	90.0	.046	107
410	92.7	.033	78
420	94.0	.027	63
440	95.7	.018	42
460	96.6	.015	35
480	97.4	.011	25
500	97.8	.010	23
540	98.2	.0075	18
600	98.8	.006	14
700	98.8	.006	14
800	99.0	.004	9

TABLE VII (Continued)

Concentration 4 x 10^{-6} Moles per Liter

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
320	96.7	.014	3500
330	96.8	.0135	3370
340	96.8	.0135	3370
350	97.0	.013	3250
360	97.2	.0125	3120
370	97.5	.011	2750
380	97.7	.0105	2650
390	97.9	.009	2250
400	98.2	.008	2000
420	98.6	.006	1500
440	99.0	.005	1050
480	99.15	.004	1000
500	99.15	.004	1000
530	99.6	.002	500
600	99.6	.002	500
650	99.6	.002	500
700	99.6	.002	500

TABLE VIII

Absorption Spectra of Nickel m-Nitrobenzoylnitromethane

Concentration 1 x 10^{-5} Moles per Liter

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
230	63.8	.195	19500
235	69.9	.155	15500
240	70.0	.154	15400
245	70.2	.152	15200
250	67.1	.177	17700
260	65.7	.1825	18250
270	69.0	.162	16200
280	76.0	.119	11900
290	81.2	.091	9100
300	84.7	.0725	7250
310	87.3	.057	5700
320	92.5	.034	3400
330	93.3	.029	2900
340	93.8	.0275	2750
350	94.2	.026	2600
360	94.8	.023	2300
370	95.2	.022	2200
380	95.6	.019	1900
390	96.0	.017	1700
400	96.6	.0145	1450
420	97.8	.009	900
440	98.3	.0075	750

TABLE VIII (Continued)

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
480	98.8	.006	600
500	99.15	.004	400
600	99.8	.0015	150
700	100	.000	0
Concentration 4 x 10^{-6} Moles per Liter			
320	96.7	.014	3500
330	96.8	.0135	3370
340	96.8	.0135	3370
350	97.0	.013	3250
360	97.2	.0125	3120
370	97.5	.011	2750
380	97.7	.0105	2650
390	97.9	.009	2250
400	98.2	.008	2000
420	98.6	.006	1500
440	98.95	.005	1050
460	99.0	.005	1050
480	99.2	.004	1000
500	99.2	.004	1000
530	99.6	.002	500
600	99.5	.002	500
700	99.5	.002	500

TABLE IX

Absorption Spectra of Nickel Acetate

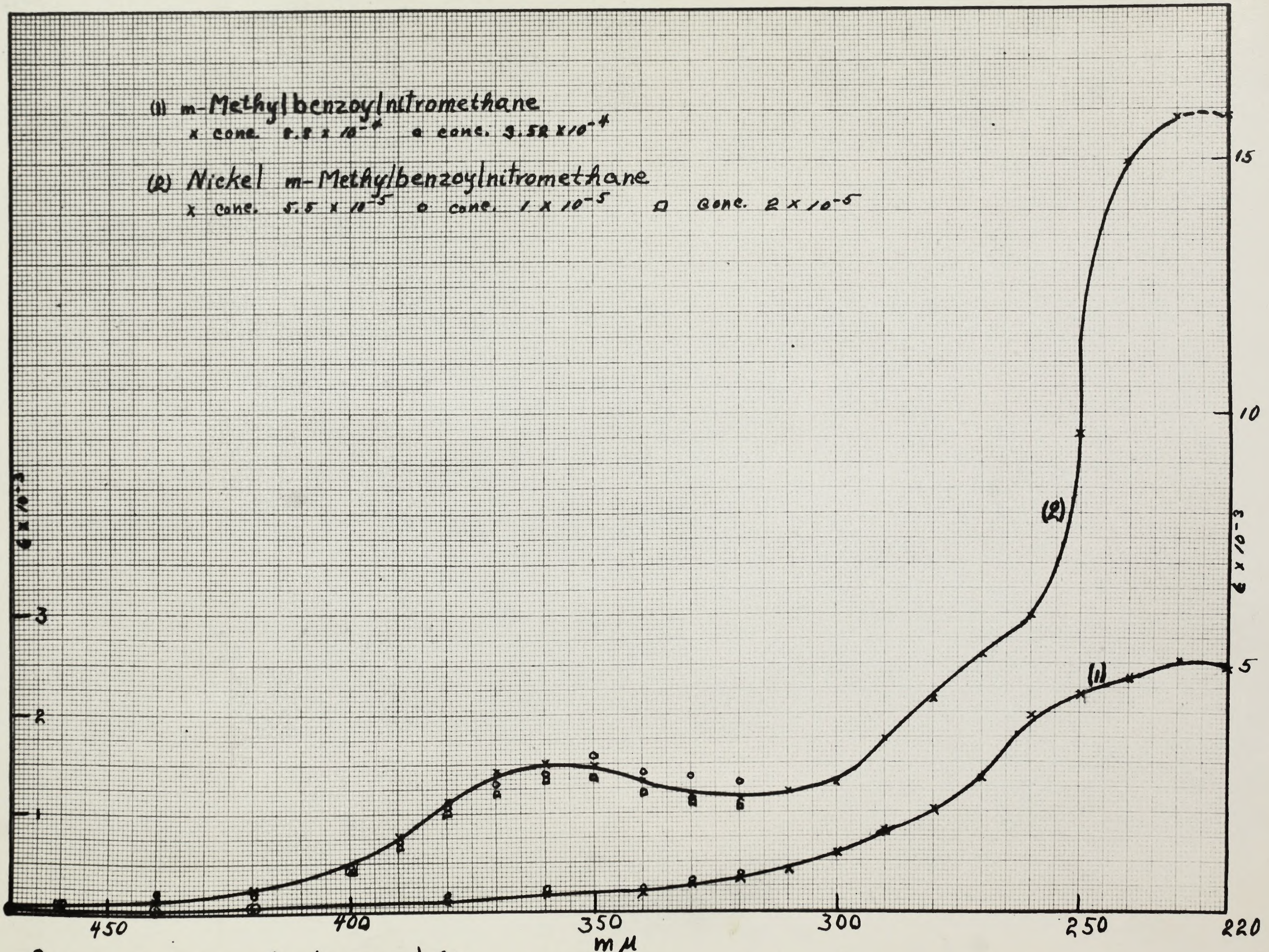
Concentration 2 x 10^{-3} Moles per Liter

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
220	5.45	1.263	632
230	25.2	.600	300
250	69.8	.156	78
260	82.0	.086	43
270	94.8	.023	11.5
280	97.0	.013	6.5
290	97.5	.011	5.5
300	97.7	.010	5
310	98.1	.008	4
320	98.5	.007	3.5
330	99.2	.004	2
340	99.2	.004	2
350	98.5	.007	3.5
360	98.5	.007	3.5
370	98.0	.008	4
380	96.8	.013	6.5
390	95.5	.020	10
400	94.8	.023	11.5
410	94.0	.027	13.5
420	95.6	.019	9.5

TABLE IX (Continued)

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
430	96.8	.013	6.5
440	97.7	.010	5
450	98.4	.007	3.5
460	98.8	.006	3
470	99.1	.004	2
500	99.4	.0025	1.25

Fig. 3



Curve (1) use ordinate on left

TABLE X

Absorption Spectra of m-Toluylnitromethane

Concentration 8.8 x 10^{-4} Moles per Liter

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
220	0.67	2.17	2454
230	.53	2.275	2540
240	.87	2.06	2340
250	1.19	1.91	2170
260	1.92	1.715	1966
270	6.5	1.187	1340
280	12.8	.897	1019
290	20.4	.690	784
300	31.2	.505	573
310	42.8	.367	405
320	51.8	.286	325
330	57.7	.238	260
340	61.8	.208	236
350	65.2	.186	211
360	69.1	.160	182
370	74.9	.126	141
380	81.3	.089	101
390	86.8	.062	70
400	90.1	.045	50
410	92.5	.034	38

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TABLE X (Continued)

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
420	93.7	.028	32
440	95.2	.021	23
460	96.5	.015	17
480	97.2	.012	13
500	98.0	.008	9
600	99.2	.004	4
700	99.6	.002	2
800	100	.000	2
Concentration 3.52 x 10^{-4} Moles per Liter			
320	75.0	.127	360
330	78.0	.107	304
340	79.3	.100	284
350	80.3	.093	264
360	82.8	.077	218
370	86.2	.063	179
380	90.1	.045	128
390	93.2	.025	71
400	94.8	.023	65
410	96.7	.017	48
420	96.8	.017	48
440	97.7	.010	28
460	98.2	.008	22

TABLE X (Continued)

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
480	98.6	.006	17
500	98.7	.006	17
540	99.0	.0045	13
600	99.5	.003	9
700	99.5	.003	9
800	99.5	.003	9

TABLE XI

Absorption Spectra of Nickel m-Toluylnitromethane

Concentration 5 x 10^{-5} Moles per Liter

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
230	16.1	.792	15840
240	17.8	.748	14960
250	33.2	.478	9560
260	50.3	.299	5980
270	55.3	.259	5180
280	60.8	.214	4280
290	67.2	.173	3460
300	74.2	.129	2580
310	76.2	.120	2400
320	77.2	.112	2240
330	76.2	.1175	2350
340	73.8	.132	2640
350	71.2	.147	2940
360	70.3	.152	3040
370	72.2	.142	2840
380	76.0	.113	2260
390	84.2	.075	1500
400	90.3	.0435	870
420	95.0	.0225	450
440	97.3	.012	240
460	98.6	.007	140

TABLE XI (Continued)

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
480	99.0	.004	80
500	99.2	.0035	70
550	99.6	.002	40
600	99.7	.002	40
650	99.8	.001	20
700	100	.000	0
Concentration 1 x 10^{-5} Moles per Liter			
320	94.1	.026	2600
330	92.8	.0275	2750
340	93.6	.028	2800
350	93.2	.0315	3150
360	93.5	.028	2800
370	94.2	.026	2600
380	95.2	.0215	2150
390	96.7	.0145	1450
400	97.9	.0085	850
420	99.2	.0035	350
440	99.2	.0035	350
460	99.5	.0025	250
480	99.2	.0035	350
500	98.5	.007	700
550	99.8	.001	100
600	99.8	.001	100
700	100	.000	0

TABLE XI (Continued)

Concentration 2 x 10^{-5} Moles per Liter

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
320	90.8	.0425	2125
330	90.2	.045	2250
340	89.2	.048	2400
350	88.2	.0545	2725
360	88.2	.0545	2725
370	89.2	.048	2400
380	91.1	.040	2000
390	93.8	.0275	1375
400	96.5	.0165	835
420	98.5	.007	350
440	98.8	.005	250
460	99.3	.003	150
480	99.3	.003	150
500	99.6	.002	100
550	100	.000	0

Fig. 4

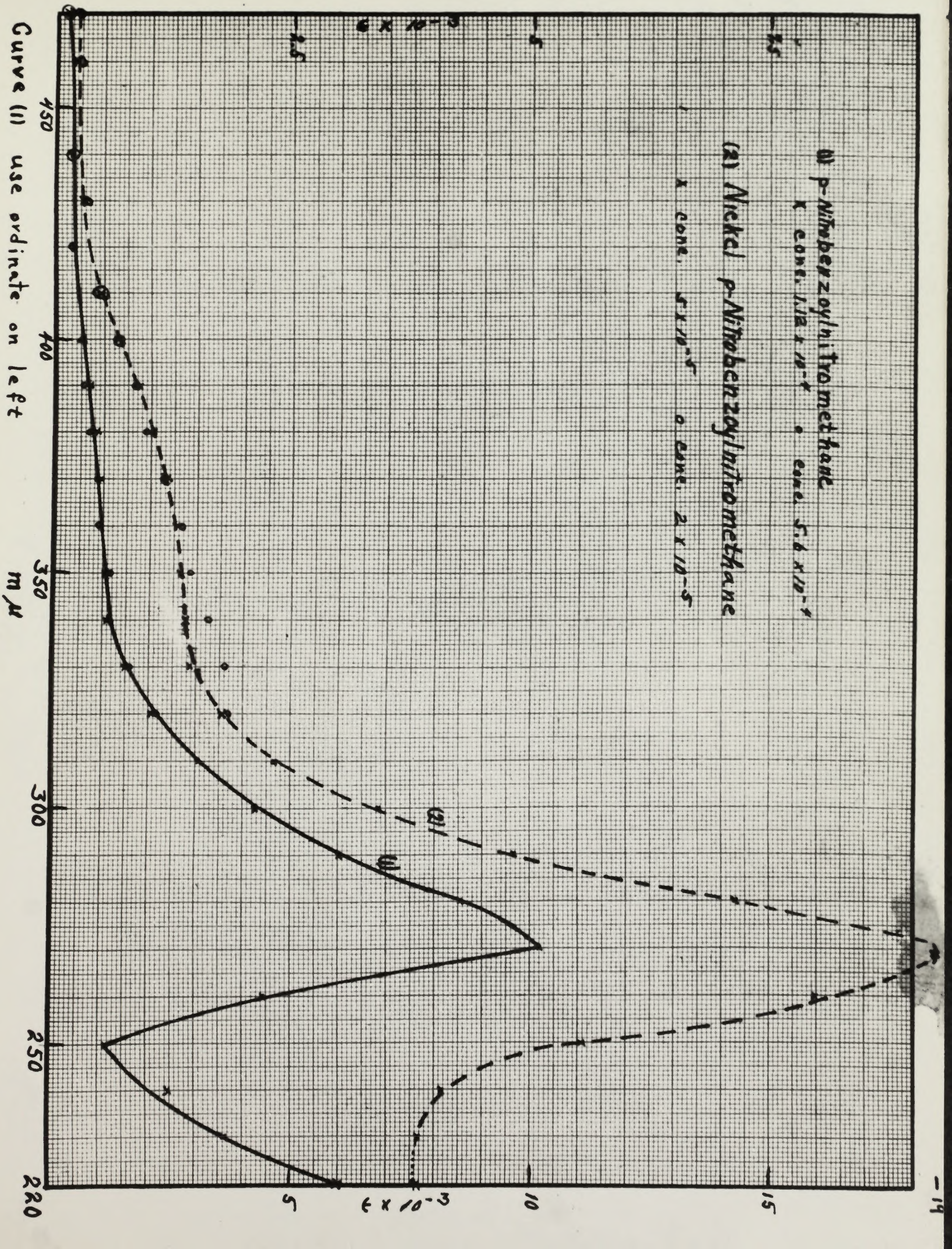

(1) p-Nitrobenzoylnitromethane
x conc. 1.12 × 10^-4 o conc. 5.6 × 10^-4
(2) Nickel p-Nitrobenzoylnitromethane
x conc. 5 × 10^-5 o conc. 2 × 10^-5
ε × 10^-3
2.5
5
7.5
(1)
(2)
450
400
350
300
250
220
m μ
5
ε × 10^-3
10
15
-19
Curve (1) use ordinate on left

TABLE XII

Absorption Spectra of p-Nitrobenzoylnitromethane

Concentration 1.12 x 10^{-4} Moles per Liter

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
220	45.2	.334	3000
230	63.0	.201	1800
240	73.2	.136	1214
250	87.8	.057	598
260	56.4	.248	2214
270	26.8	.572	5107
280	33.1	.479	4276
290	46.6	.332	3000
300	57.8	.238	2125
310	67.2	.172	1535
320	77.5	.114	1016
330	82.6	.083	742
340	85.4	.068	608
350	86.9	.062	562
370	88.3	.054	482
380	90.1	.046	410
390	91.8	.037	330
400	93.5	.029	258
410	94.5	.024	214
420	95.2	.022	186
440	95.6	.019	168
480	97.2	.013	116

TABLE XII (Continued)

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
520	98.7	.007	62
560	99.5	.002	16
600	99.5	.002	16
	Concentration 5.6×10^{-4} Moles per Liter		
320	25.5	.595	1062
330	35.8	.447	800
340	43.7	.358	639
350	48.8	.331	591
360	54.0	.262	468
370	60.0	.222	400
380	65.3	.186	332
390	70.0	.153	273
400	74.2	.129	230
410	77.5	.111	200
420	79.6	.098	175
440	82.4	.084	150
480	88.6	.053	94
520	95.5	.020	36
560	97.0	.009	16
600	98.0	.008	14

TABLE XIII

Absorption Spectra of Nickel p-Nitrobenzoylnitromethane

Concentration 5 x 10^{-5} Moles per Liter

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
230	41.3	.3825	7650
235	41.7	.379	7580
240	38.8	.407	8140
245	34.2	.462	9240
250	27.9	.555	11100
260	15.9	.798	15960
270	11.2	.952	19040
280	19.3	.715	14300
290	33.0	.482	9680
300	45.8	.343	6860
310	58.3	.233	4660
320	66.3	.178	3560
325	70.2	.152	3040
330	71.8	.143	2860
340	73.2	.136	2720
350	73.8	.132	2640
360	74.8	.126	2520
370	76.3	.117	2340
380	78.5	.105	2010
390	81.8	.087	1740
400	86.0	.065	1300

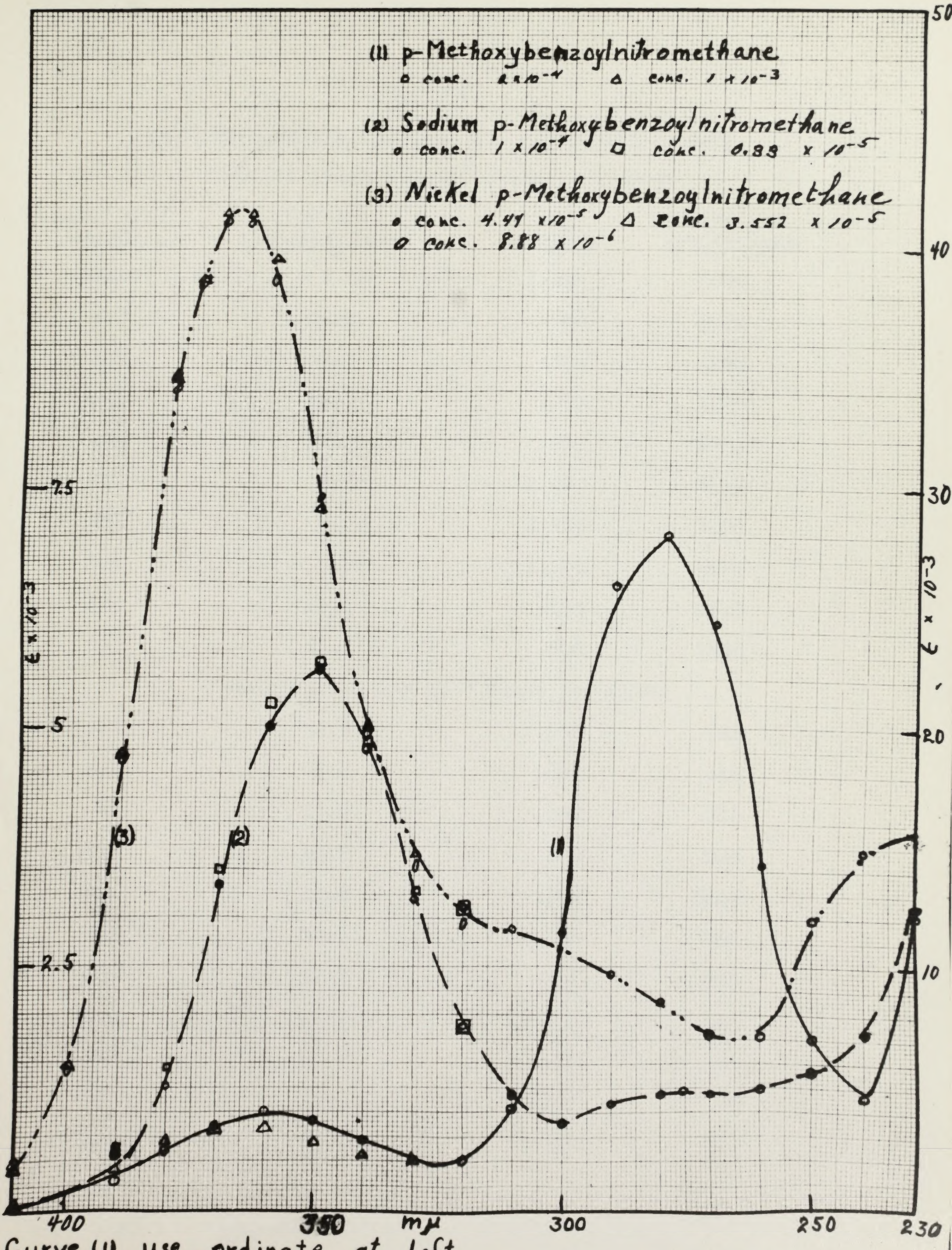
TABLE XIII (Continued)

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
420	92.7	.028	560
480	96.8	.014	280
540	98.9	.0045	90
600	99.3	.003	60
700	99.3	.003	60
800	99.3	.003	60
900	99.3	.003	60
1000	99.3	.003	60
Concentration 2 x 10^{-5} Moles per Liter			
320	84.5	.0725	3625
325	85.8	.066	3300
330	84.75	.072	3600
340	86.2	.0645	3225
350	87.5	.0575	2875
360	88.5	.053	2650
370	89.9	.046	2300
380	91.2	.038	1900
390	92.7	.033	1650
400	94.2	.026	1300
420	96.5	.0155	775
480	98.5	.0065	320
540	99.6	.002	100

TABLE XIII (Continued)

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
600	99.8	.001	50
700	99.8	.001	50
800	99.8	.001	50
900	99.8	.001	50
1000	99.8	.001	50

Fig. 5



Curve (1) use ordinate at left

TABLE XIV

Absorption Spectra of p-Methoxybenzoylnitromethane

Concentration 2 x 10^{-4} Moles per Liter

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
220	7.80	1.12	5600
230	24.8	.605	3025
240	58.7	.232	1160
250	44.3	.353	1765
260	19.5	.717	3585
270	6.10	1.22	6100
280	3.52	1.454	7270
290	5.08	1.294	6470
300	25.6	.594	2870
310	62.2	.205	1020
Concentration 4 x 10^{-4} Moles per Liter			
320	62.8	.202	505
330	61.8	.207	518
340	51.6	.287	718
350	42.8	.363	908
360	39.8	.402	1005
370	45.1	.340	850
380	57.3	.242	605
390	77.3	.112	280
400	90.8	.042	105
410	97.0	.013	33
420	98.7	.006	15

TABLE XIV (Continued)

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
440	99.5	.002	5
480	100	.000	0
Concentration 1 x 10^{-3} Moles per Liter			
330	31.5	.500	500
340	26.3	.580	580
350	19.0	.720	720
360	14.8	.830	830
370	14.9	.827	827
380	19.8	.702	702
390	38.2	.419	419
400	70.0	.154	154
410	90.2	.044	44
420	96.5	.015	15
440	98.7	.007	7
460	99.3	.004	4
480	99.3	.004	4
500	99.7	.002	2
520	100	.000	0

TABLE XV

Absorption Spectra of Sodium p-Methoxybenzoylnitromethane

Concentration 1 x 10^{-4} Moles per Liter

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
230	5.96	1.225	12250
240	19.00	.729	7290
250	26.00	.586	5860
260	32.2	.491	4910
270	33.5	.475	4750
280	33.3	.476	4760
290	36.5	.437	4370
300	41.3	.384	3840
310	35.1	.454	4540
320	17.5	.754	7540
330	5.25	1.280	12800
340	1.22	1.910	19100
350	.57	2.24	22400
360	1.0	2.0	20000
370	4.56	1.343	13430
380	28.0	.552	5520
390	74.6	.127	1270
400	94.3	.025	250
450	100	.000	0

TABLE XV (Continued)

Concentration 0.33 x 10^{-5} Moles per Liter

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
320	55.8	.253	7590
330	36.7	.437	13110
340	22.5	.648	19340
350	16.9	.771	23130
360	19.7	.702	21060
370	33.2	.463	13890
380	63.3	.197	5910
390	89.4	.048	1440
400	97.2	.012	480
450	99.5	.002	60
500	99.5	.002	60

TABLE XVI

Absorption Spectra of Nickel p-Methoxybenzoylnitromethane

Concentration 4.44 x 10^{-5} Moles per Liter

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
230	20.3	.691	15650
240	21.9	.656	14750
250	26.6	.576	11990
260	46.5	.333	7480
270	47.0	.328	7410
280	41.8	.378	8520
290	37.0	.432	9700
300	33.1	.480	10800
310	30.7	.512	11550
320	29.7	.551	12520
330	22.5	.645	14500
Concentration 3.552 x 10^{-5} Moles per Liter			
320	36.6	.443	12470
330	30.2	.522	14690
340	19.4	.712	20040
350	9.15	1.037	29190
360	3.92	1.408	39620
365	3.35	1.475	41520
370	3.35	1.475	41520
380	5.585	1.233	34690
390	21.4	.672	18910

TABLE XVI (Continued)

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
400	62.8	.202	5970
410	87.2	.059	1660
420	94.5	.024	675
440	98.6	.006	169
460	99.5	.0025	70
Concentration 3.553×10^{-5} Moles per Liter			
490	99.6	.003	84
600	99.9	.001	28
675	99.8	.002	56
690	100	.000	0
800	99.7	.0025	70
Concentration 8.88×10^{-6} Moles per Liter			
320	79.9	.1025	11880
330	74.8	.126	14190
340	66.8	.174	19590
350	55.3	.263	29610
360	45.2	.343	38560
370	43.0	.366	41220
380	49.7	.303	34120
390	68.2	.167	18800
400	88.8	.053	5850
410	96.25	.017	1910
420	97.8	.008	900

TABLE XVI (Continued)

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
440	99.0	.0045	506
460	99.2	.004	450
490	99.2	.004	450
600	99.5	.0025	281
675	99.2	.004	450
690	99.5	.0025	281
800	99.1	.0045	506
900	99.1	.0045	506

Fig. 6

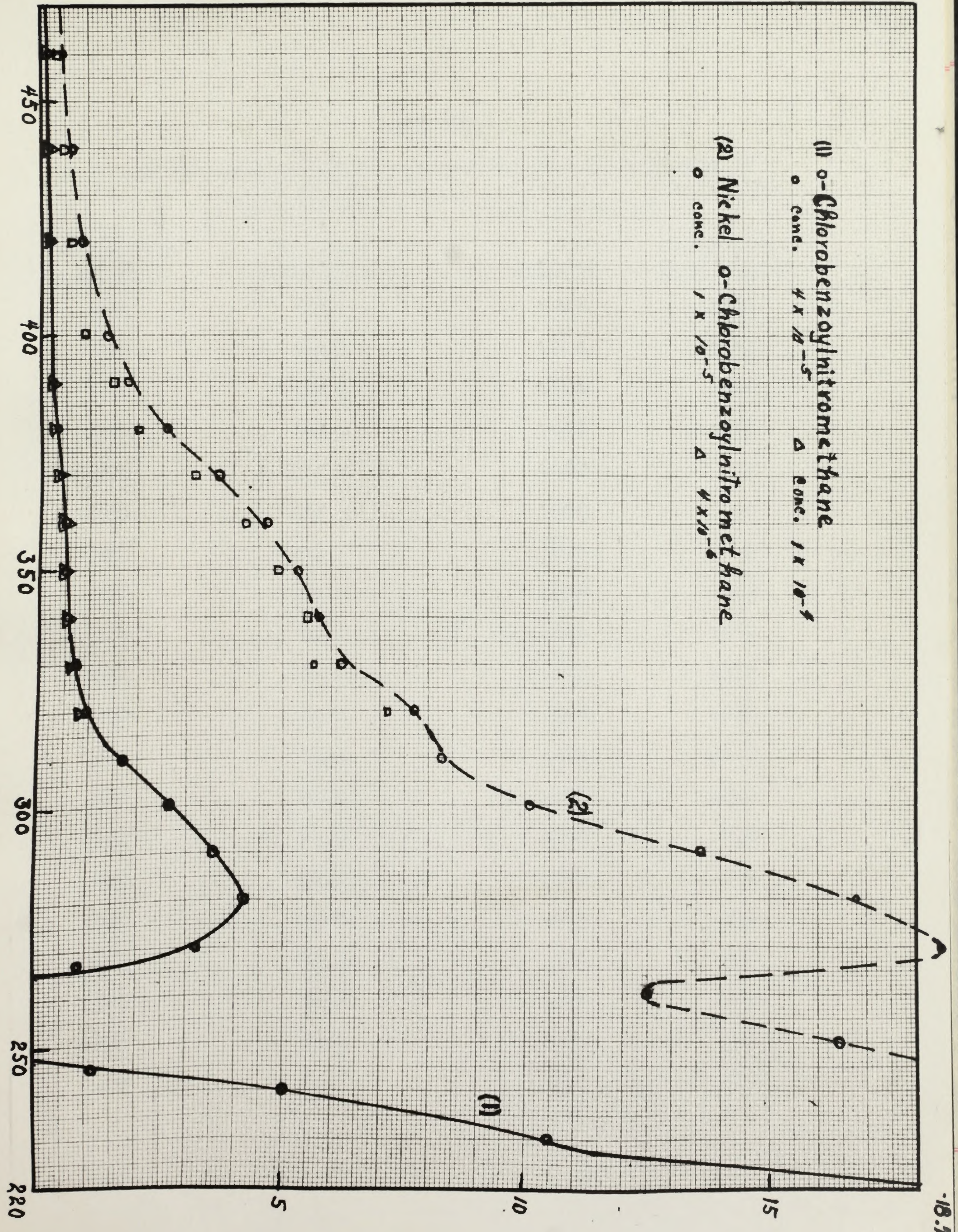

(1) o-Chlorobenzoylnitromethane
o conc. 4 x 10⁻⁵ Δ conc. 1 x 10⁻⁴
(2) Nickel o-Chlorobenzoylnitromethane
o conc. 1 x 10⁻⁵ Δ 4 x 10⁻⁶
(1)
(2)
450
400
350
300
250
220
5
10
15
18.9

TABLE XVII

Absorption Spectra of o-Chlorobenzoylnitromethane

Concentration 4 x 10^{-5} Moles per Liter

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
220	17.5	.756	18900
230	38.3	.418	10450
240	62.9	.202	5050
245	89.5	.047	1175
250	100	.000	0
260	100	.000	0
265	100	.000	0
267	92.5	.034	850
270	74.3	.128	3200
280	67.8	.168	4200
290	71.9	.143	3550
300	78.2	.106	2650
310	84.5	.073	1825
320	92.0	.036	900
330	93.8	.027	700
340	94.7	.023	550
350	95.5	.020	500
360	96.2	.016	400
370	96.9	.013	325
380	97.2	.012	300

TABLE XVII (Continued)

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
390	97.7	.010	250
400	97.7	.010	250
420	98.1	.007	175
440	98.7	.006	150
460	98.7	.006	150
500	98.9	.005	125
550	99.0	.0045	112
600	99.2	.004	100
700	99.8	.0015	38
800	100	.000	0
	Concentration 1 x 10^{-4} Moles per Liter		
320	82.8	.083	830
330	86.0	.065	650
340	88.0	.054	540
350	89.8	.047	470
360	91.4	.038	380
370	93.0	.032	320
380	93.8	.027	270
390	94.9	.023	230
400	95.5	.020	200
420	96.3	.016	160
440	97.2	.012	120

TABLE XVII (Continued)

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
460	97.3	.012	120
500	98.0	.008	80
550	98.0	.008	80
600	98.2	.007	70
700	99.2	.004	40
800	99.5	.002	20

TABLE XVIII

Absorption Spectra of Nickel o-Chlorobenzoylnitromethane

Concentration 1 x 10^{-5} Moles per Liter

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
230	34.5	.456	45600
235	41.4	.382	38200
240	50.2	.299	29900
250	68.5	.164	16400
260	75.0	.125	12500
270	65.0	.187	18700
275	65.6	.178	17800
280	67.7	.168	16800
285	70.5	.152	15200
290	73.1	.136	13600
300	79.2	.101	10100
310	82.5	.083	8300
320	83.5	.077	7700
330	86.8	.062	6200
340	87.5	.0575	5750
350	88.5	.053	5300
360	89.8	.047	4700
370	91.8	.037	3700
380	94.1	.0265	2650
390	95.8	.018	1800
400	96.9	.0135	1350
410	97.6	.0115	1150

TABLE XVIII (Continued)

Wavelength in mu	Per Cent Transmission	Density	Extinction Coefficient
420	98.0	.0085	850
440	98.5	.0065	650
460	99.0	.0045	450
480	99.5	.0025	250
500	99.7	.002	200
520	100	.000	0
Concentration 4 x 10^{-6} Moles per Liter			
320	93.3	.0285	7125
330	95.0	.0225	5625
340	95.1	.022	5500
350	95.5	.0195	4900
360	96.2	.017	4250
370	97.1	.0125	3125
380	98.1	.008	2000
390	98.8	.006	1500
400	99.2	.0035	875
410	99.3	.003	725
420	99.5	.0025	625
440	99.7	.002	500
460	99.8	.0015	350
480	100	.000	0

III. CONCLUSIONS

The reaction between benzaldehyde or a substituted benzaldehyde and nitromethane under the influence of potassium hydroxide proceeded very smoothly. However, it was observed that the potassium salts of the carbinols prepared by this reaction were somewhat soluble in methyl alcohol. Therefore, it was necessary that the quantity of solvent used be kept at a minimum to ensure complete precipitation of the potassium salt. Previous investigators (11) reported yields of 85% for the reaction of one mole of benzaldehyde with one mole of nitromethane using a total of 400 ml of methyl alcohol as the solvent. In this work it was found that increasing the amount of methyl alcohol used to 465 ml decreased the yield to 34%.

Oxidation of the carbinols obtained through the condensation of nitromethane with benzaldehyde or a substituted benzaldehyde resulted in poor yields of nitroketones. The highest yield was 33% for the oxidation of phenyl nitromethyl carbinol; the lowest, 3% for the oxidation of m-tolyl nitromethyl carbinol. Oxidation by acid dichromate was generally successful, but chromium trioxide in glacial acetic acid was necessary in the case of m-tolyl nitromethyl carbinol. Earlier investigators (11) reported a yield of 70% for the oxidation of phenyl nitromethyl carbinol by potassium dichromate in an acid medium.

Many of the compounds described in this Thesis were prepared here for the first time. These include m-tolyl nitromethyl carbinol, p-methoxyphenyl nitromethyl carbinol,

m-nitrophenyl nitromethyl carbinol, p-nitrophenyl nitromethyl carbinol, m-toluylnitromethane, m-nitrobenzoylnitromethane, p-methoxybenzoylnitromethane, o-chlorobenzoylnitromethane, and the copper and nickel chelated complexes of the preceeding ketones as well as the copper and nickel chelated complexes of benzoylnitromethane and p-nitrobenzoylnitromethane.

The nickel complexes were found to be more stable towards acids and bases than the copper complexes. Whereas the nickel complexes were stable in cold dilute sodium hydroxide and decomposed only in the hot, the copper complexes decomposed readily in the cold. This characteristic held true in the case of dilute mineral acids. There was no difference between the behavior of the complexes of the substituted benzoylnitromethanes towards acids and bases and the behavior of the complexes of benzoylnitromethane towards acids and bases.

It was impossible to determine any correlation between the substituent on the benzene ring in the series of ketones, copper chelated complexes, or nickel chelated complexes and the solubility of these series of compounds in various organic solvents. It can only be said that of the chelated complexes, the nickel and copper m-toluylnitromethane are soluble in the greatest number of solvents, and the copper and nickel p-nitrobenzoylnitromethane are soluble in the least number of solvents. Pyridine, of all the solvents studied, is the only one capable of dissolving all the copper and nickel chelated compounds.

Copper benzoylnitromethane was of great interest because it occurred in two forms, one green and one brown. Originally it was thought that this color change might be due to cis-trans isomers of the compound. All primary alcohols investigated, with the exception of n-propyl alcohol, brought about the transformation of the brown form to a green form when the brown form was heated in the alcohol. Sec.-alcohols, acetone, chloroform, benzene, ether, et cetera converted any green form to the brown form. Quantitative measurements showed that the green forms were due to solvation of the copper benzoylnitromethane by these primary alcohols. Since the copper complex solvated with methyl alcohol was quite stable, and since the copper complex solvated with butyl alcohol tended to lose its alcohol of solvation readily, it is indicative that the alcohols with higher molecular weights form less stable complexes with copper benzoylnitromethane.

Tests to determine the ability of other copper and nickel chelated complexes to become solvated by the various solvents tested, proved that, of the metal complexes investigated, only the copper benzoylnitromethane is solvated by primary alcohols.

Much is now known about the structure of metal complexes and the bonds connecting the metal atom to the rest of the molecule. As a review it should be noted that the energy of a covalent bond is largely the energy of resonance of two electrons between two atoms. In addition, of two orbitals in an atom the one that can overlap more with an orbital of

another atom will form the stronger bond with that atom. Since the s orbital is spherically symmetrical, it can form a bond equally well in any direction. The three p orbitals, however, are directed at right angles to one another and are concentrated in these directions. Due to this concentration, it is found that a p bond will have a strength 3 times as an s bond; 1.732 to 1, using 1 as the value of the strength of an s bond.

There are four orbitals available in the valence shell of the carbon atom. These are the 2s and the three 2p orbitals. These orbitals individually are not used directly in bond formation. The wave function of this system is found by adding together the wave functions of its component parts; the function of the normal state being that one which minimizes the energy of the system as a whole. This normal function is the one that makes the bond strengths the greatest. A linear combination of s and p orbitals is found to have a strength greater than any s of p bond alone, the best strength of an s-p hybrid being as great as 2. These four sp bonds form an angle of 109° 28' with each other and are directed towards the corners of a regular tetrahedron.

The first-row elements have only these four valence orbitals. For the second-row elements the s and p orbitals are the stable ones, but there also exists the five 3d orbitals in the M shell. Although less stable than the s and p orbitals, these d orbitals are available for bond formation if necessary. For heavier atoms than those in the second row, much use is made of the d

orbitals in bond formation. It is, however, the d orbitals of the shell with total quantum number one less than the valence shell which are of greatest significance for bond formation. For the atoms of the first transition group (the iron group) there is little difference in the energy of the 3d orbitals and the 4s and 4p orbitals. The same holds true for the 4d, 5s and 5p orbitals of the palladium group, and the 5d, 6s and 6p orbitals of the platinum group.

The maximum bond strength of a d orbital has been found to be 2.236. The bond formed by d-s-p hybridization has a strength of 3. Therefore, when stable d orbitals are available, much stronger bonds can be formed than with s and p orbitals alone, for which the maximum bond strength is 2.

In a complex of bivalent nickel, the twenty-six inner electrons of the nickel atom can be placed in the 1s, 2s, three 2p, 3s, three 3p, and four of the 3d orbitals. This leaves the fifth 3d orbital, the 4s orbital, and the three 4p orbitals available for bond formation. Hybridization of these orbitals results in four strong bonds, with a strength of 2.694, directed towards the corners of a square. These bonds are coplanar. This configuration is typified by compounds such as nickel benzylmethylglyoxime, which has been separated into cis and trans isomers, and nickel dithio-oxalate, on which x-ray studies have proved the coplanar arrangement. Since the coplanar bivalent nickel complex having dsp^2 bonds has only four 3d orbitals available for the eight unshared 3d

electrons, the electrons must form four pairs, the molecule being diamagnetic.

Bivalent nickel in a complex involving only the 4s and 4p orbitals distributes the eight electrons among the five 3d orbitals in such a way as to leave two electrons unpaired. This leaves the complex with a theoretical magnetic moment of 2.83 Bohr magnetons. From these facts, it is seen that assignment of nickel complexes to the tetrahedral and square coplanar classes can be made by magnetic measurements.

Nickel diacetyldioxime, nickel ethylxanthogenate, nickel dithiocarbamate and many others (20) have been found to be diamagnetic and assigned the square coplanar structure.

On the other hand, nickel acetylacetone, $(Ni(NH_3)4)_2SO_3$ and $(Ni(N_2H_2)_2)(NO_2)_2$ are paramagnetic with magnetic moments between 2.6 and 3.2 Bohr magnetons. In these complexes, the atoms attached to the nickel presumably are arranged tetrahedrally.

Willis and Mellor (22) have reported that it is conceivable that the difference of stability of square and tetrahedral nickel complexes is in some cases very small. Under the influence of solvent molecules, certain square coplanar nickel complexes are partially converted to a tetrahedral configuration, so that the solution of the complex shows a paramagnetic moment whose magnitude depends upon the proportion of the molecules so converted.

Thus the factors which determine whether the diamagnetic

square or the paramagnetic tetrahedral configuration will be assumed by a nickel complex cannot be stated precisely. However, as stated earlier, all complexes belonging to the class that has the nickel atom linked to four oxygen atoms have, up to the present time, been found to be paramagnetic, presumably with a tetrahedral arrangement of the atoms. Figs. 1 and 5 reveal that the spectra of the sodium salts of benzoylnitromethane and p-methoxybenzoylnitromethane bear great resemblance to those of the nickel chelated complexes. The spectra of the chelates have somewhat higher extinction coefficients and are displaced slightly towards higher wavelengths. It would be expected that the sodium salts of the other substituted benzoylnitromethanes would show similar characteristics when compared to the spectra of the nickel chelated complexes. The paramagnetic complexes of nickel do not show any bands in the region 400 to 480 millimicrons that can be attributed to the nickel atom. From Figs. 1-6 it is evident that none of the spectra of the nickel complexes investigated showed any bands in the region that could be attributed to nickel. From these three facts ((1) the nickel atom attached to four oxygen atoms, (2) the similarity of the spectra of the sodium salts of benzoylnitromethane and p-methoxybenzoylnitromethane and the nickel complexes of the same, and (3) no bands attributable to nickel present in the spectra of the nickel complexes) a paramagnetic tetrahedral structure can tentatively assigned to the nickel chelated complexes of benzoylnitromethane and its homologues.

The problems of assigning a structure to the copper complexes of benzoylnitromethane and it homologues is a relatively easier problem. Bivalent copper would be expected to form four bonds of dsp^2 type rather than tetrahedral sp^3 bonds (strength 2.694 instead of 2). However, bivalent copper possesses one electron more than bivalent nickel. Usually the electron would be assigned to the fifth 3d orbital, leaving this orbital unavailable for bond formation. No loss of energy would be occasioned, however, by placing this electron in the third 4p orbital of the copper atom and using the 3d orbital for bond formation. Each of the five orbitals in question (one 3d, one 4s, three 4p) is occupied by a shared pair or by the single unshared electron. The interaction energy of a shared pair with the copper atom is the same as that of a single unshared electron. Accordingly, the greater strength of dsp^2 bonds than sp^3 bonds is the determining factor. The bivalent copper complex with a coordination number 4 will have a square coplanar rather than a tetrahedral configuration.

Copper acetylacetone, copper benzoylacetone, copper disalicylaldoxime, and copper dipropionylmethane have, by x-ray studies, been shown to possess the square coplanar configuration (20,24). Therefore, the square coplanar configuration may be assigned to copper benzoylnitromethane and its homologues.

The absoprtion of light by organic or inorganic molecules is due to a resonator or group of resonators. The resonators

may be coupled or separated in the molecule; if coupled, they may be coupled directly (cumulation), or coupled through a single bond (conjugation). For the most part, resonating groups of atoms are unsaturated and contain an incomplete inner shell of electrons. To each of these resonating groups there may be assigned a wavelength (frequency) factor, but it is difficult, if not impossible at the present time, to predict from these values the absorption bands of a complex molecule unless each resonator is independent and well shielded from the other resonating systems.

It is customary to ascribe to that resonating group in the molecule responsible for the color and main absorption bands the name "chromophore". The groups generally included in lists of organic chromophores are the ethylene, carbonyl, azo, nitro, azomethine, sulfoxide, quinone, nitroso, ketene, polyethenylene, fluvene, and phenyl groups.

Chromophoric changes may be resolved into two effects, intensity and wavelength (frequency) shifts, and are described as follows:

(1) Hyperchrome: An increase in the extinction value of the absorption band. The intensity of color increases.

(2) Hypochrome: A decrease in the extinction value of the absorption band. The intensity of color decreases.

(3) Bathochrome: A shift in the absorption band towards the red (higher wavelength, lower frequency). The color deepens.

(4) Hypsochrome: A shift in the absorption bank towards

the blue (lower wavelength, high frequency). The color lightens.

In addition to the resonating groups or chromophores, there are a number of groups which are known as auxochromes. Although these do not always produce resonance in themselves, they exert a powerful effect on the resonance of other systems. In addition to the usual positive auxochromes, OH, OR, NH_2, NR_2, NHR, which cause hyperchromic and bathochromic effects in positive ions with a coordinated resonating group, there are negative auxochromes, NO, NO_2, CO, CN, SO_2, which produce the same effects in negative ions with a coordinated resonating nucleus. For complicated resonating structures, there is little hope for a complete analysis of the system. However, the absorption spectrum can be used to fingerprint certain important parts of complicated structures.

Figs. 1 - 6 show the absorption spectra of benzoylnitromethane and its homologues and the absorption spectra of the nickel chelated compounds of benzoylnitromethane and its homologues. The principal chromophores present in these compounds are the nitro group, the carbonyl group, and the benzene ring. The methoxyl group, the chloro group, and the methyl group are the auxochromes present.

The nitro-derivatives of organic compounds all show absorption bands which are due to the -N O group. This group is a powerful resonator which produces bands in the near ultraviolet and visible regions of the spectrum. Nitrobenzene shows a very intense band at 294 millimicrons, extending from

the visible (evidenced by its natural yellow color) until well down into the ultraviolet.

The carbonyl group in organic molecules causes strong absorption in the ultraviolet. Acetone in absolute alcohol shows a strong band at 270.6 millimicrons. An increase in the size of the alkyl radicals in the ketone causes hyperchromic and hypsochromic shifts. An even greater effect is produced on the carbonyl absorption band as a result of tautomeric equilibrium between enol and keto forms. The reduction, by the addition of alkali, of the extinction coefficient of the absorption band produced by acetone and other carbonyl compounds is explained by the formation of a salt with the hydroxyl hydrogen of the enol form.

Benzene, because of its unusual structure, may be considered an endless conjugated chain, in that the bonds continue in conjugation as one goes around the ring. In the ultraviolet at 200 millimicrons, benzene shows intense absorption.

It should be pointed out that electronically alike substances may be assumed to give similar spectra. Nonconjugate chromophores in the same molecule produce essentially the added effects of the two separate groups, whereas conjugated chromophores produce a marked bathochromic and hyperchromic effect.

The work of Lambert and Beer was of primary importance in developing the relationship between absorption and length of light path and that between absorption and concentration. These relationships may be expressed as

$$E = \log I_0/I = kcd$$

where E = extinction or the ratio of the incident to the transmitted light. Lambert's Law states that the extinction, E, is a linear function of the thickness of the solution or solids, d. Beer's Law says that the extinction is a function of the concentration, c. Beer's Law has been used as a tool to determine a change in molecular species with a change in concentration of a compound. The case of keto-enol equilibrium is a problem of this type. The percentage enol changes with changing concentration. Thus at different concentrations, a keto-enol compound will have different extinctions. This deviation from Beer's Law has been used many times as proof of keto-enol equilibrium and similar tautomeric shifts.

Curve (3), Fig. 1 is the spectrum of benzoylnitromethane. It shows a band of e = 6625 at 240 millimicrons and a smaller band of e = 1260 at 350 millimicrons. The band of lower intensity at 350 millimicrons may be due to an enolic form or enolic ion of benzoylnitromethane. Beer's Law is not followed in this range, and, as would be expected, with decreasing concentration of ketone, the extinction coefficient increases.

Curve (2), Fig. 1 increases the certainty that the band at 350 millimicrons is due to enolate ion. The sodium salt of benzoylnitromethane must exist as an enolate ion. The band in question shows a very considerable hyperchromic shift in going from benzoylnitromethane to its sodium salt. The peak in the ultraviolet region disappears, and general increasing absorption

of the nitro and phenyl groups takes its place.

The spectra of p-methoxybenzoylnitromethane and its sodium salt (curves (1) and (2), Fig. 5) show a band in the same region (350-360 millimicrons) that can be attributed to the enolic form of the ketone. In going from the ketone to its sodium salt, there again is a very considerable hyperchromic shift. Beer's Law is not followed in the ketone (two molecular species present). Thus the entire pattern is very similar to the case of benzoylnitromethane and its sodium salt. The effect of the p-methoxyl group (the auxochrome present) is to increase the band at 350 millimicrons from e = 12980 in sodium benzoylnitromethane to e = 22400 in the spectra of sodium p-methoxybenzoylnitromethane. Again in the case of p-methoxybenzoylnitromethane, there is a band, this time at 270 millimicrons, attributable to the absorption of the nitro and carbonyl groups.

The spectrum of m-nitrobenzoylnitromethane (curve (1), Fig. 2), m-toluylnitromethane (curve (1), Fig. 3), p-nitrobenzoylnitromethane (curve (1), Fig. 4), and o-chlorobenzoylnitromethane (curve (1), Fig. 6) all show a very definite band in the ultraviolet (250-270 millimicrons) that can be attributed to the nitro and carbonyl groups. At a lower wavelength (220-240 millimicrons) that is the absorption to be expected in compounds containing the benzene ring. These compounds show no band at 350 millimicrons. In the two cases where there was a maximum at 350 millimicrons, Beer's Law was not followed. In these last four ketones Beer's Law is followed. This leads to the

hypothesis that benzoylnitromethane and p-methoxybenzoylnitromethane exist in an absolute alcohol solution partly in the enol form and partly in the keto form. The other ketones in the series exist then only in the keto form.

The spectrum of the individual ketones in the series exhibit certain pecularities. As yet, it is not possible to find a clear-cut correlation between the substituents on the benzene ring (induction or resonance effects) and the extinction coefficients or wavelengths (frequencies) as found in the absorption spectra. Further investigation along these same lines may well result in a correlation of this type. Another investigation that might profitably be pursued is to obtain the spectra of the sodium salts of these ketones varying the amount of excess sodium ethoxide present. This should lead to a set of curves with a band at 350 millimicrons having different extinction coefficients. The exact excess of ethoxide ion necessary to prevent alcoholysis of the ionic form of the ketones could be found from a set of these curves. It is possible that the 20-fold excess of ethoxide ion used in this work was not enough to prevent a small amount of alcoholysis from taking place. A quantitative method of establishing the per cent enol present in a solution of a ketone of this type could probably be developed.

It is evident, on studying the problem, that a comparison of the spectrum of one of the ketones with its nickel chelate must take into account the fact that the nickel chelate has

twice as many resonating groups per molecule as its parent ketone. Therefore, a molecule of nickel chelate would be expected to show twice the absorption attributable to the different resonating groups. This explains the reason why it is necessary to compare the one-half value of the extinction coefficient of the nickel chelate with the extinction coefficient of the ketone.

All the spectra of the nickel chelates studied, with the exception of nickel p-nitrobenzoylnitromethane (curve (2), Fig. 4), show a general absorption starting at 250 millimicrons and increasing with lower wavelengths. It appears from the slope of the curve of the spectrum of nickel p-nitrobenzoylnitromethane that here too the same absorption will occur at lower wavelengths. This absorption would, of course, be due to the benzene ring contained in the molecules of these compounds. The nickel p-nitro-, m-nitro-, and o-chlorobenzoylnitromethane spectra have a band of high intensity in the range 260-270 millimicrons (curve (2), Fig. 4, curve (2), Fig. 2, curve (2) Fig. 6). In the cases of the p- and m-nitro- complexes, there is an obvious explanation. Each molecule of these complexes contains four nitro groups, twice the number present in the other complexes. Since the absorption band in question has been ascribed to the presence of nitro and carbonyl, this 2-fold increase in the number of nitro groups present in the molecule should be reflected by this high extinction coefficient. The equally high extinction coefficient in the spectra of nickel o-chlorobenzoylnitromethane is as yet unexplained. Perhaps

study of the ortho effect might clear up this point.

The magnitude of the extinction coefficients in the spectra of the nickel chelates of the band in the range 350-370 millimicrons in the order of decreasing value is as follows: nickel p-methoxybenzoylnitromethane greater than nickel benzoylnitromethane greater than nickel o-chlorobenzoylnitromethane greater than nickel m-toluylnitromethane greater than nickel p-nitrobenzoylnitromethane equal to nickel m-nitrobenzoylnitromethane. However, the correlation, if any exists, between the inductive or resonance effects of the substituents on the benzene ring of the molecules and the magnitude of the extinction coefficients has yet to be found.

Comparison of the spectra of the series of ketones and the spectra of their nickel chelates reveal some fairly general trends. In all cases, the spectra of the nickel complexes show a hyperchromic and bathochromic effect for the band located in the range 350-370 millimicrons and a hypochromic and hypsochromic effect for the band in the range 240-270 millimicrons (with the exception of the nickel m-toluylnitromethane and nickel o-chlorobenzoylnitromethane) when compared with the spectra of the parent ketones. Future investigation in this field should determine the exact significance of these shifts and develop a correlation between the magnitude and direction of these shifts and the induction or resonance effects of the substituent groups on the benzene ring in the various compounds.

None of the nickel chelated complexes of the series inves-

tigated follows Beer's Law closely. This variation from Beer's Law may be explained by any one of a number of as yet unknown factors. It might be that in absolute alcohol solution the nickel chelated complexes dissociate to ionic forms. This would mean that the apparent change in concentration would not be the actual change in concentration. The actual change in concentration would depend upon the per cent dissociation, and it would not be expected that Beer's Law would be followed. Another possibility is cis-trans isomerization in these compounds. Again future work should find a solution to this problem. Molecular weight determinations of these complexes both in the solid state and in solution would be of particular interest.

Curve (3), Fig. 2 is the spectrum of nickel acetate in absolute alcohol. Simple aliphatic acids and esters are transparent down to 220 or 230 millimicrons. This then explains the absorption in the lower range of the ultraviolet. Since the extinction coefficient along the rest of the spectra is very small, it is evident that the nickel atom plays a very unimportant role, if any at all, in the spectra of the nickel chelated complexes of benzoylnitromethane and its homologues.

IV. SUMMARY

The following list of nitroketones was prepared by condensation of the appropriate aromatic aldehyde with nitromethane, as first described by Thiele (2) and then adapted by Holleman (11), followed by oxidation of the nitroalcohol so formed:

Benzoylnitromethane
m-Nitrobenzoylnitromethane
m-Toluylnitromethane
p-Methoxybenzoylnitromethane
p-Nitrobenzoylnitromethane
o-Chlorobenzoylnitromethane

Copper and nickel chelated complexes were then prepared from these nitroketones. The copper complex of benzoylnitromethane exhibited unusual solvation effects. Primary alcohols coordinate with brown copper benzoylnitromethane to form a green complex. This green complex can be reconverted to the brown form by heating in solvents such as acetone, chloroform, benzene and ether. n-Propyl alcohol was the only promary alcohol investigated that does not form a green complex with copper benzoylnitromethane. The copper complexes of the homologues of benzoylnitromethane and the nickel complexes of benzoylnitromethane and its homologues do not undergo this type of solvation reaction.

The nickel complexes of benzoylnitromethane and its homologues were found to be somewhat more stable towards acids

and bases than their copper counterparts. There was no appreciable difference in the behavior of the metal complexes of benzoylnitromethane from that of the metal complexes of the substituted benzoylnitromethanes towards acids and bases.

The solubilities of two series of metal complexes were investigated. Copper and nickel m-toluylnitromethane were soluble in the greatest number of solvents, while copper and nickel p-nitrobenzoylnitromethane were soluble in the least number of solvents. There is no correlation between substitution in the benzene ring of these compounds and their solubilities.

Tentatively a square planar (dsp^2 bonds) configuration has been assigned to all the copper chelated complexes investigated. As yet all x-ray diffraction work has shown that all copper complexes possess this square planar structure. The nickel complexes have been assigned the paramagnetic tetrahedral (sp^3 bonds) structure. This is confirmed by the spectra of the nickel chelated complexes and the spectra of the sodium salts of the organic addenda being similar, the structure of the complexes being such that the nickel atom is attached to four oxygen atoms, and that no bands attributable to the nickel atom are found in the spectra of the nickel chelated complexes.

The spectra of benzoylnitromethane and its homologues, nickel benzoylnitromethane and its homologues, sodium benzoylnitromethane, sodium p-methoxybenzoylnitromethane and nickel acetate in absolute alcohol solutions were recorded and studied.

The bands occurring in the region 240-270 millimicrons were attributed to the presence of nitro and carbonyl groups. Absorption starting at 240 millimicrons and increasing with lower wavelengths was attributed to the presence of the benzene ring. A band in the region 350-370 millimicrons was attributed to the presence of the enolic form of benzoylnitromethane and its homologues. The deviation from Beer's Law of the spectra of benzoylnitromethane and its homologues was also attributed to the presence of keto and enol forms of the ketones.

There is no correlation at present between the magnitude of the molar extinction coefficients of the spectra studied and the induction or resonance effects of the substituents on the benzene ring of the compounds investigated. Similarly no correlation has as yet been developed between these inductive and resonance effects and the bathochromic and hypsochromic shifts for the spectra of the nickel complexes when compared with the spectra of their parent ketones.

The nickel atom plays a very unimportant role, if any at all, in the spectra of the nickel chelated complexes of benzoylnitromethane and its homologues.

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